Clarence R. Robbins

Chemical and Physical Behavior of Human Hair

5th Edition

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With 233 Figures

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To my wife, Gene for 50 years of hope, making every day meaningful for me. To my father, an example for me and an inspiration to many. To my mother, who struggled with health problems throughout her long life but accepted it with grace. To my daughter Laurie and her husband T.J. and little Griffin; to my son, Mark; to my brother John and his family and to my "little sister" Becky and to Ken and his family and to my many other relatives and friends who help to make life meaningful for me.

I would like to dedicate this fifth edition to five colleagues and friends who have had a very positive influence on my life and/or my career in science. To John Wright, who initiated my interest in chemistry; to Bill Truce, who taught me to work as an independent scientist; to George Scott, my mentor in keratin fiber science; to Charles Reich, a colleague who kept me on my toes scientifically, but who unfortunately passed away about a year ago and to Glenn King a wonderful friend who passed away just a few days ago.

Preface to the Fifth Edition

Nearly 9 years have passed since the writing of the fourth edition and much progress has been made in that time span. Identification and classification of the chromosomes and genes involved in the important IF (intermediate filament) and KAP (keratin associated proteins) proteins of human hair and some of the genes involved in different forms of alopecia and hair abnormalities has occurred. Many of the SNPs of different genes in natural hair color and hair fiber size and shape and the geographic influence on these genes and properties have also been made. Our understanding of the distribution of different proteins in the fiber and its control of hair fiber curvature has increased dramatically. Methods development has also increased at a rapid pace. For example, a new hair curvature (most important single fiber property of hair) method has been described and applied to the scalp hair of more than 2,400 different persons in more than 20 different countries. Our understanding of hair growth, hair breakage, the torsional behavior of hair and the mechanisms of important oxidative reactions (chemical bleaching and sunlight degradation) in human hair has also improved greatly.

This edition contains expanded data and more comprehensive data bases with statistical analyses for hair fiber diameters, hair densities (hairs/cm^2), ellipticity, incidence of hair graying, male pattern alopecia, female pattern alopecia versus age, and comparisons of most of these properties among different geo-ethnic groups and males versus females. Sections on the effects of pregnancy and the menopause on hair fiber and assembly properties have also been expanded as well as a new Chapter providing definition for most of the important cosmetic hair assembly properties and how these properties are influenced by changes in single fiber properties in general and as a function of age.

Clermont, USA — Clarence R. Robbins

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Abbreviations

C	Curvature
D	Diameter
S	Stiffness
E	Static charge
E_S	Stretching modulus or Young's modulus
E_B	Bending modulus
E_T	Torsional modulus
R	Rigidity
G	Stiffness coefficient
SAXS	Small angle x-ray scattering
ESCA or XPS	X-ray photoelectron spectroscopy
Wnt proteins	A family of signaling molecules that regulate biological processes
Lef1	Lymphocyte enhancement factor
BMP	Bone morphogenetic proteins
Shh	Sonic hedgehog
SNP	Single nucleotide polymorphism
IF	Intermediate filament
KAP	Keratin associated protein
CMC	Cell membrane complex
UV	Ultraviolet light
MPA	Male pattern alopecia
FPA	Female pattern alopecia
18-MEA	18-methyleicosanoic acid
SLS	Sodium lauryl sulfate
SDS	Sodium dodecyl sulfate
DHT	Dihydrotestosterone

Chapter 1
Morphological, Macromolecular Structure and Hair Growth

Abstract At or near its surface, hair fibers contain a thick protective cover consisting of six to eight layers of flat overlapping scale-like structures called cuticle or scales which consists of high sulfur KAPs, keratin proteins and structural lipids. The cuticle layers surround the cortex, but the cortex contains the major part of the fiber mass. The cortex consists of spindle-shaped cells that are aligned parallel with the fiber axis. Cortical cells consist of both Type I and Type II keratins (IF proteins) and KAP proteins. Coarser hairs often contain one or more loosely packed porous regions called the medulla, located near the center of the fiber. The cell membrane complex, the "glue" that binds or holds all of the cells together, is a highly laminar structure consisting of both structural lipid and protein structures.

Hair fibers grow in cycles consisting of three distinct stages called anagen (growth), catagen (transition) and telogen (rest). Each stage is controlled by molecular signals/regulators acting first on stem cells and then on the newly formed cells in the bulb and subsequently higher up in differentiation in the growing fiber. The effects and incidence of hair growth and hair loss (normal and diseased) for both males and females are described in detail. Molecular structures controlling hair fiber curvature (whether a fiber is straight or curly) and the effects of the different structural units of the fiber on stress–strain and swelling behavior are described in detail.

1.1 Introduction

Since writing the fourth edition, several significant findings have occurred regarding the morphology, the growth and development, and the structure of human scalp hair fibers. Our knowledge of hair growth, development and formation both at the cellular and the molecular levels has continued to increase at a rapid rate and our understanding of the origin of fiber curvature has increased considerably. For example, recent evidence demonstrates more of a bilateral type structure in human hair fibers as curvature increases providing different types of cortical

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structures on the inside of a curl vs. the outside, analogous to wool fiber. Additional details of the surface structure, that is the epicuticle and the cuticle cell membranes have been uncovered providing a better understanding of the surface of hair fibers and the organization and makeup of the three cell membrane complexes that binds all of the hair cells together. Significant findings regarding the lipid composition of hair, its importance to barrier functions, to the isoelectric point and its potential for stress strain involvement have been added.

Important additions to the sections on male and female pattern alopecia have been made including incidence vs. age and affected regions of the scalp. Additional information on hair diameter and hair density (hairs/cm^2) changes with age, hair density in different regions of the scalp and variation by geo-racial group (linking geographic origin and its effects on genetics with race). The effects of pregnancy on scalp hair are also described in greater detail than in prior editions.

Human hair is a keratin-containing appendage that grows from large cavities or sacs called follicles. Hair follicles extend from the surface of the skin through the stratum corneum and the epidermis into the dermis, see Fig. 1.1. Hair provides protective, sensory and sexual attractiveness functions. Hair is characteristic of all

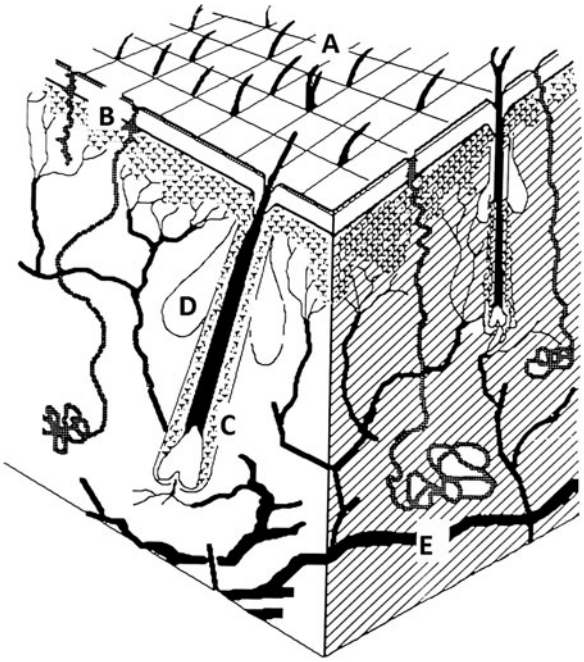

Fig. 1.1 A section of human skin illustrating a hair fiber in its follicle as it emerges through the skin and how it is nourished

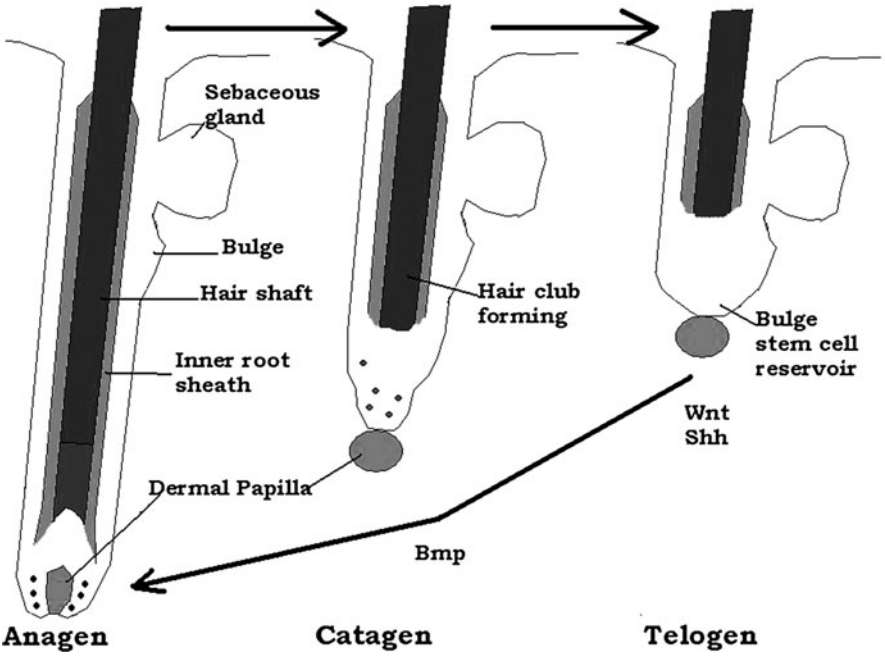

Fig. 1.2 Schematic illustrating the three stages of growth of human hair fibers

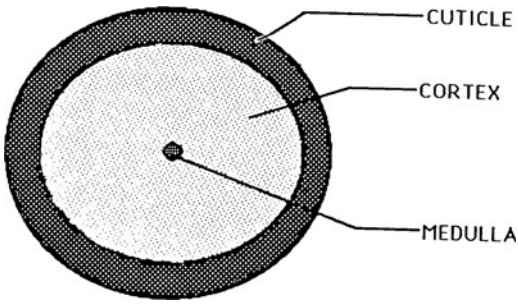

Fig. 1.3 Schematic diagram of a cross section of a human hair fiber

mammals and in humans grows over a large percentage of the body surface. Regardless of the species of origin or body site, human hair grows in three distinct stages and has certain common structural characteristics. These three cyclical stages of hair fibers are called anagen (growing stage), catagen (transition stage) and telogen (resting stage), see Fig. 1.2.

Morphologically, a fully formed hair fiber contains three and sometimes four different units or structures. At or near its surface, hair contains a thick protective covering consisting of one or more layers of flat overlapping scale-like structures called cuticle or scales see Fig. 1.3. The cuticle layers surround the cortex, but the

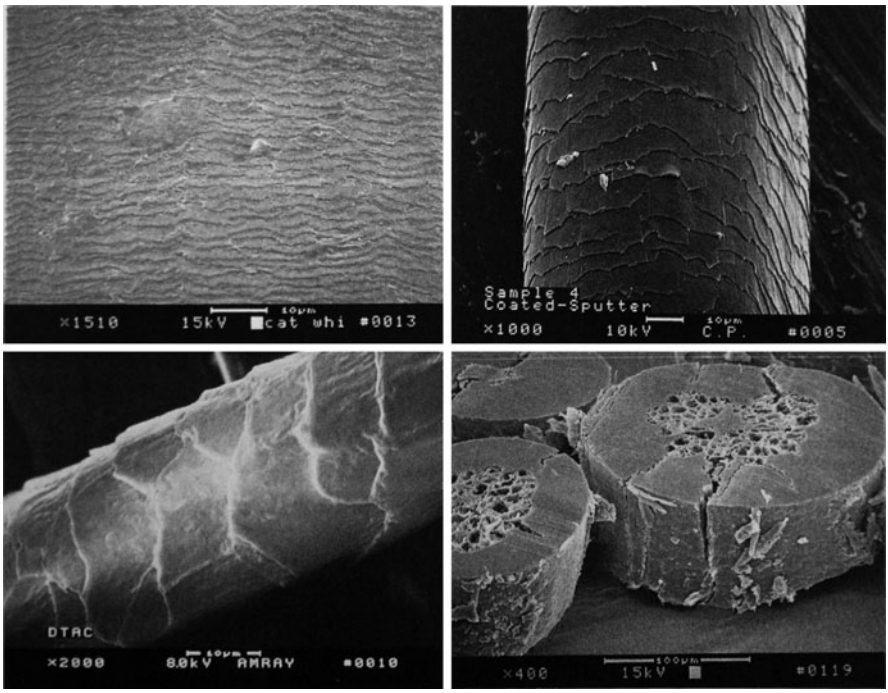

Fig. 1.4 Hair fibers from different mammalian species. *Upper left* is an SEM of a cat whisker (1510 X). *Upper right* is an SEM of a human hair fiber (1000 X). *Lower left* is an SEM of a wool fiber (2000 X). *Lower right* is an SEM of sections of horse tail fiber (400 X)

cortex contains the major part of the fiber mass. The cortex consists of spindle-shaped cells that are aligned parallel with the fiber axis. Cortical cells contain many of the fibrous proteins of hair. Coarser hairs often contain one or more loosely packed porous regions called the medulla, located near the center of the fiber. The fourth important unit of structure is the cell membrane complex the "glue" that binds or holds all of the cells together.

These structures with the exception of the medulla are in all animal hairs, the medulla only in coarser hairs. Figure 1.4 contains scanning electron micrographs (SEMs) of four mammalian species taken at different magnifications. These micrographs demonstrate the cuticle structure of a cat whisker, a wool fiber, a human hair, and a horsetail hair. The cross-sections of the horsetail hair reveal the cortex and the multiple porous channels or regions of the medulla characteristic of coarse hairs, but generally absent from fine animal hairs such as fine wool fiber.

Although this book is concerned with hair fibers in general, the primary focus is on human scalp hair and this chapter is concerned mainly with the morphology, the macromolecular structure and the growth of this unique natural fiber.

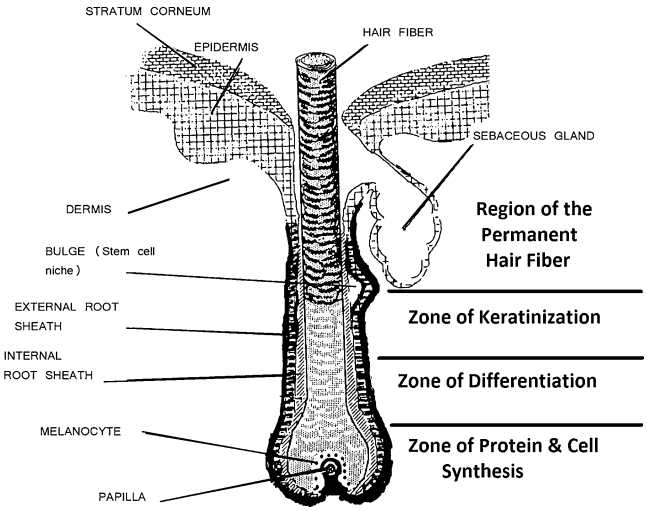

Fig. 1.5 Pilosebaceous unit with a hair fiber in its follicle and the zones of protein and cell synthesis, differentiation, keratinization and the region of the permanent hair fiber as the fiber emerges through the scalp

1.2 General Structure and Growth

The schematic diagram of Fig. 1.5 illustrates an active growing human hair fiber inside the follicle, which is the sac that originates in the subcutaneous tissue of the skin and contains the hair fiber with several surrounding structures involved in its growth. The dermal papilla, located near the center of the bulb is involved in important growth functions during anagen (Fig. 1.2). The basal layer that produces hair cells nearly surrounds the bulb. Melanocytes that produce hair pigment also exist within the bulb close to the dermal papilla. Blood vessels (Fig. 1.1) carry nourishment to the growing hair fiber deep within the skin at the base of the bulb. Figure 1.6 illustrates other important active layers of the growing fiber in the follicle.

The human hair fiber beneath the skin can be divided into several distinct zones along its axis (Fig. 1.5). The zone of biological synthesis and orientation resides at and around the bulb. This zone is sometimes divided into a lower region called cell proliferation or cell matrix. Moving upward in the growing fiber is the region of cell differentiation which leads into the zone of keratinization, where stability is built into the hair structure by the formation of cystine linkages [1]. The next zone that begins below the skin line and eventually emerges through the skin surface is the region of the permanent hair fiber. The permanent hair fiber consists of fully formed dehydrated cornified cuticle, cortical and sometimes medullary cells, but always the cell membrane complex which acts like a natural adhesive, binding the hair cells together.

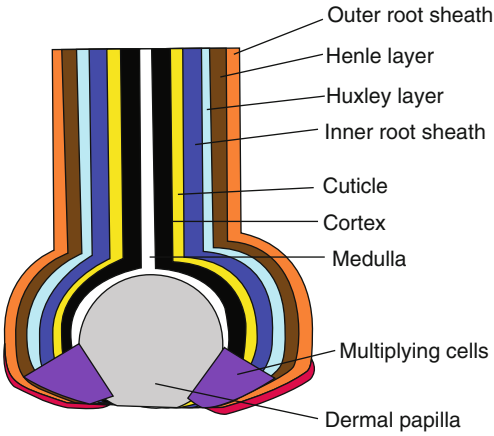

Fig. 1.6 Schematic of an active hair bulb with a hair fiber illustrating the important layers with regard to growth

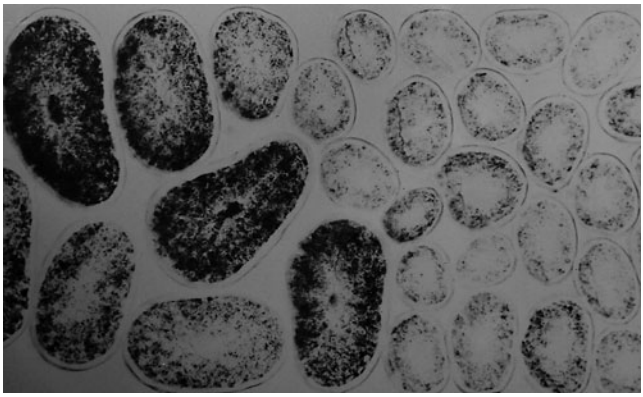

Fig. 1.7 Light micrograph of scalp hair fiber cross sections, illustrating varying fiber cross-sectional size, shape, and pigmentation. Note: lack of pigment in the cuticle

The major emphasis in this book is on the chemistry, structure, and physics of the permanent zone of the human hair fiber and as indicated; the primary focus is on human scalp hair as opposed to hair of other parts of the body.

Randebrock [2] suggested that the diameter of human scalp hair fibers varies from 40 to 120 μm. Others provide a somewhat larger range varying from about 20 to 125 μm. The low values for this latter estimate are undoubtedly due to the inclusion of hair of infants and young children. For adult hair we estimate the variation from means of subjects to be primarily between 45 and 110 μm. The range for individual hairs on individual scalps can exceed these values. Figure 1.7 illustrates the range in fiber diameters and cross-sectional shapes of hairs from five Caucasian adults. For a more complete discussion of hair fiber diameter see the next section and also Chap. 9 and the review by Bogaty [3] and the references therein.

1.2.1 Variation in Fiber Diameter on Different Parts of the Head

Most of the work in the scientific literature is on scalp hair from the vertex or the crown area, although hair from other regions of the scalp is sometimes used. Garn [4] citing others and his own work stated that scalp hair is finest at the temples and most coarse at the sideburns on "normal" scalps. "Normal" scalp usually means pre-alopecia or before the phenomenon of balding begins. The lower sideburns are actually beard hair which is coarser than scalp hair. Tolgyesi et al. [5] demonstrated that beard hair contains a higher amount or higher percentage of hairs with medulla. Beard hair is also more elliptical and it has more irregular cross-sectional shapes and lower disulfide content (cross-link density) than human scalp hair [5].

As indicated, for adults, the mean diameter (from the vertex or crown areas of the scalp) usually ranges from about 45 to about 110 μm and the diameter shows large differences among neighboring hairs on the same head, ranging from a factor of less than 1.4 to more than 2.0 on adult Caucasian women [6]. Garn is essentially in agreement with Yin et al. [6] on these ranges on an individual scalp, claiming as early as 1948 that on the same scalp neighboring hairs may vary by more than a factor of 2. Hair on different regions of the scalp grows at different rates. DeBerker et al. [7] determined that on "normal" scalps, hair grows slowest on the temples (0.39 mm/Day males) and faster on the vertex (0.44 mm/Day males) where it grows coarser. Additional data on growth rates is described later in this chapter.

Three distinct regions (cuticle, cortex and medulla) containing different types of cells are generally apparent in cross sections of fully formed human hair fibers from most parts of the body (see Figs. 1.3, 1.7 and 1.8). After brief discussions on the functions of hair, hair growth/hair loss and treatments for hair loss, the remainder of this chapter focuses on the structures of these three types of cells and the intercellular binding material (cell membrane complex) of human scalp hair.

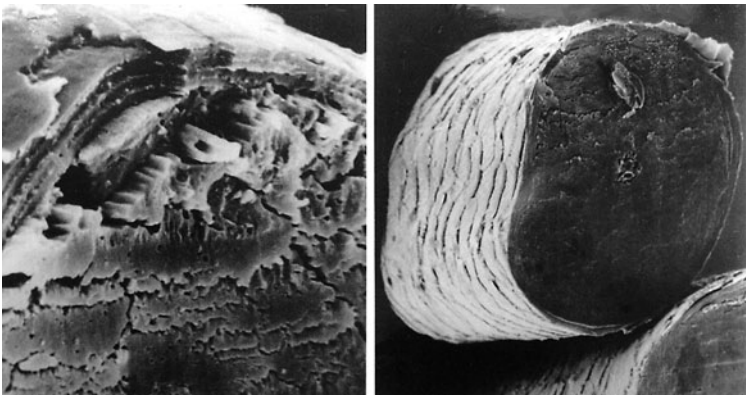

Fig. 1.8 Treated hair fibers cross sectioned with a microtime. *Right*: Note cuticle, cortex, and medulla. *Left*: Note the cuticle layers

1.2.2 Functions of Hair on Different Parts of the Body

Human scalp hair provides both protective and cosmetic or adornment functions. Scalp hair protects the head from the elements by functioning as a thermal insulator. Hair also protects the scalp against sunburn, other effects of light radiation and mechanical abrasion. Hair on parts of the body other than the scalp provides related protective and adornment functions. The adornment function of eyebrows is to the beholder. However, eyebrows also inhibit sweat and prevent extraneous matter from running into the eyes. In addition, eyebrows protect the bony ridges above the eyes, and assist in communication and in the expression of emotion.

Eyelashes are also important to adornment. Eyelashes protect the eyes from sunlight and foreign objects, and they assist in communication. Nasal hairs filter inspired air and retard the flow of air into the respiratory system, thus allowing air to be warmed or cooled as it enters the body. Hair on other parts of the anatomy serves related functions. A general function of all hairs is as sensory receptors, because all hairs are supplied with sensory nerve endings. The sensory receptor function can enhance hair in its protective actions.

1.3 Hair Growth

This discussion on hair growth is considered in two parts:

Follicular/hair apparatus development in the fetus and
Hair follicle cycling or the growth of hairs in the follicle before and after birth

1.3.1 Development of the Follicular/Hair Apparatus with its Essential Structures

Follicular/hair apparatus development in the fetus determines the number and distribution of follicles with their growth structures and the ultimate size of hair fibers thereafter. It includes the length that hair fibers can grow to on all different parts of the body at different stages of life such as the relatively long hairs of the scalp with their long anagen period and the relatively short hairs of the eyebrows with their short anagen. The mesoderm directs the ectodermal cells on how to respond via molecular signals that interact with receptor sites for the normal formation of hair follicles and their contents [8–10]. Several different molecular species have been implicated in the process of hair follicle formation including, Wnt proteins [10–12], noggin [11, 12], lymphoid enhancer-binding factor 1 (LEF-1) [10, 13], sonic hedgehog (shh) [9, 12, 14], beta-catenin [13, 15] and bone morphogenic protein (BMP) [12]. A helpful and concise review describing details of

this information is by Alonso and Fuchs [12]. In 2003, Fuchs and coworkers [11] demonstrated that two molecular signals, Wnt proteins and noggin together can influence immature stem cells to form hair follicles and their internal components. What is so fascinating is that these same stem cells can form either hair follicles or epidermis, but with Wnt protein and noggin signals originating from different parts of the skin and working together, these stem cells produce an activated transcription factor and ultimately hair follicles with their essential structures.

According to Fuchs, this process is multi-step along these lines:

- Wnt protein stabilizes B-catenin increasing its concentration in stem cells
- Noggin inhibits BMP leading to LEF-1 production
- B-Catenin activates LEF-1 (which controls gene activity)
- LEF-1 down-regulates a Gene for the protein E-Cadherin
- Lower levels of E-Cadherin reduce cell adhesion structures and initiates formation of
- Epithelial Buds for follicle formation

Too much E-cadherin (triggers cell adhesion ingredients) can interfere with the downward growth of the stem cells to form a hair follicle. However, with the optimal amount of E-cadherin the stem cells are loosened to the most favorable extent allowing them to grow downward to form a hair follicle with its different cellular structures. At the time of birth approximately five million hair follicles will have been formed over the entire human body, but no additional hair follicles are formed after birth [13]. Research on some of the genes involved in hair loss is described in Chap. 3.

1.3.2 Hair Follicle Cycling and Hair Growth

Generally around the fifth fetal month, the follicles and their growth machinery have been developed, although not entirely mature. Each individual hair after birth is programmed to grow in cycles involving three distinct stages (see Fig. 1.2). These growth stages of the hair fiber are partly controlled by chemical messengers including Wnt proteins (Wnt) [8, 14, 16, 17] and Sonic hedgehog (shh) [9, 16, 18] that stimulate stem cells in the bulge and induce new anagen. Factors that are known to maintain anagen are SGK3 [12, 19] and Msx2 [12, 20]. Androgens (hormones produced by the adrenals and the sex glands stimulate the activity of male sex glands and male characteristics) also play a role in hair development. As indicated in the introduction, the three stages of growth are called anagen, catagen and telogen:

1. The anagen stage, or the actual growing stage, is characterized by intense metabolic activity in the hair bulb. For scalp hair, this activity generally lasts 2–6 years producing hairs that grow to approximately 100 cm in length (~3 ft);

Fig. 1.9 "Three women," by Belle Johnson. Taken about 1900. Hair generally grows to a maximum length of about 3 ft; however, specimens over 5 ft in length have been documented (Reprinted with permission of the Massillon Museum, Massillon, Ohio)

however, human scalp hair longer than 150 cm (~5 ft) is frequently observed in long hair contests (see Fig. 1.9), indicative of a longer anagen period.
Terminal (children or adult) hair does grow at slightly different rates on different regions of the scalp. For example, hair grows at approximately 14-cm/year (~5.5 in./year) on the vertex or the crown area of the scalp of Caucasian females adults; at a slightly slower rate (~13 cm/year) in the temples and generally at even slower rates on other body regions (e.g., ~10 cm/year) in the beard area.

2. The catagen stage or the transition stage lasts for only a few weeks. During catagen, metabolic activity slows down, and the base of the bulb migrates upward in the skin toward the epidermal surface. Molecular regulators that promote the transition from anagen to catagen are: Growth factors (FGF5 and EGF1) and neurotrophins (BDNF, p53, TGFβ1 and BMPRIa) [12].

3. Telogen or the resting stage also lasts only a few weeks (generally 4–8). At this stage, growth has stopped completely and the base of the bulb has atrophied to the point at which it approaches the level of the sebaceous canal.

At the onset of a new growth cycle, a new hair begins to grow beneath the telogen follicle, pushing the old telogen fiber out. The telogen fiber is eventually shed. Sometimes a latency period or a lag time occurs between hair shedding and the subsequent anagen period. This lag time has been called the "hair eclipse phenomenon" [9]. St. Jacques et al. [9] attributed this lag time to a dysfunction involving early shedding and delayed anagen initiation or stunted hair growth between the two anagen phases. The hair eclipse may occur in telogen effluvium (abnormal shedding) associated with new alopecia, post-partum alopecia, seasonal alopecia, alopecia areata or even shedding associated with seborrheic dermatitis or dandruff. St. Jacques et al. [9] suggested that local growth factors or other mediators that are either missing or deficient may be involved in this condition. The effects of antidandruff agents on abnormal shedding are described in Chap. 6 in the section on dandruff.

Kishimoto et al. [17] demonstrated that at the beginning of each growth cycle or new anagen period one or two stem cells that originate in the bulge (Fig. 1.5) are induced by chemical messengers to produce or re-grow the lower portion of the follicle (down to the zone of protein and cell synthesis Fig. 1.5) that ultimately produces hair cells leading to a new hair fiber. Among the more important of these molecular signals or factors essential to follicle induction for hair cycling are Wnt proteins (Wnt) [8, 10, 17] and Sonic hedgehog (shh) [9, 14, 16, 18]. Kishimoto et al. [17] determined that Wnt signaling is essential for maintaining the hair inductive activity of the dermal papilla. Signaling by Wnts and shh is essential for new anagen and these regulators somehow act to initiate formation of the growth region of hair follicles and the production of cells that have the potential to form hair fibers. The cells continue to divide in the matrix of the bulb (zone of protein and cell synthesis) with virtually no differentiation until molecular signals initiate movement upward in the follicle and then differentiation begins in the zone of differentiation see Fig. 1.5. Zhu et al. [21] reported that the concentration of B1-integrin appears to control whether a cell moves upward to differentiate (lower concentration) or continues to divide in the matrix of the bulb. Lin et al. [22] identified notch proteins in differentiating cuticle and cortical cells and suggested these proteins are also involved in differentiation.

The newly formed hair cells near the base of the bulb at the dermal papilla (cell matrix) move upward into the zone of differentiation and the melanocytes in that same region produce the hair pigment or pigments that are incorporated into each growing hair fiber. This pigment is incorporated into the cortical and medullary cells of scalp hair by a phagocytosis mechanism as suggested by Piper [23].

Kulessa et al. [24] found that bone morphogenetic proteins (BMP's) function in differentiation. This fact has been demonstrated by inhibition of BMP's with Noggin which produces an absence of acidic hair keratins (IF proteins) in cuticle and cortical cells and an absence of tricohyalin protein in the medulla.

The expression of several transcription regulators of differentiation (Hocx13, Foxn1, Msx1 and Msx 2) are also reduced to low levels.

Lef1 (lymphocyte enhancement factor) is activated in the initial cortex and is a factor that directly controls the transcription of hair shaft genes in protein production [24, 25]. This activity of Lef1 in hair cycling suggest that Lef1 and BMP's cooperate in hair shaft differentiation and contrasts with the antagonistic action of these two regulators during early follicle development in the embryo as shown by DasGupta and Fuchs [25].

Among the first proteins formed in differentiating cortical cells are the intermediate filament proteins. A single Type 1 (acidic) and a Type II (basic-neutral) intermediate filament protein combine to form helical dimers. These low sulfur dimers aggregate and two dimers combine to form tetramers. The tetramers interact and become connected longitudinally to form sub-filaments sometimes called protofilaments important subunits of the cortex. Human hair has at least 9 Type I and 6 Type II intermediate filament proteins see the section in this Chapter entitled *The Cortex*. Rogers [26] described that after the intermediate filament proteins, the glycine-tyrosine rich proteins, the KAP's (Keratin Associated Proteins) 6, 7 and 8 and finally the sulfur rich proteins are formed. Rogers also suggested that the KAP's 1 and 5 are among the last cortical cell proteins to be expressed.

The cortex forms before the cuticle with the helical dimers forming and aggregating and combining as described to initiate formation of the intermediate filaments. The types and relative amounts of the intermediate filament proteins (IF's) to KAP's help determine the type of cortex that forms, such as orthocortex, mesocortex or paracortex see *The Origin of Hair Fiber Curvature* in this chapter.

The cuticle forms higher up in the follicle and its cystine rich proteins are largely from the KAP5 and KAP10 families [26]. The site and synthesis of 18-methyl eicosanoic acid of the cuticle cell membrane complex is not known, but is believed to be very high up in the follicle during the latter stages of synthesis and differentiation.

After formation of cortical and cuticle cells, the cells remain bound by desmosomes, tight junctions and gap junctions. These will ultimately be replaced by cell membrane complex. During protein synthesis, hair proteins are kept in a reduced state with virtually no disulfide cross-links. During the final stages, the cells move upward into the zone of keratinization (Fig. 1.5) where disulfide and iso-peptide cross-links are formed and dehydration occurs. Disulfide bonds form through a mild oxidative process over a length of several hundred micrometers, and ultimately the permanent hair fiber is completed. Rogers [26] suggested that the keratinization zone is about 1,000 μm long (about ten times the diameter of a coarse human scalp hair fiber). The hair cells must be nearly completely filled with proteins as they are cross linked in about 48 h as they pass through the zone of keratinization [26].

The maturation process (over an individual's life span) for scalp hairs in humans is controlled by androgens and other chemical messengers. Prenatal hairs usually originate in the third or fourth month of fetal life. In humans, prenatal hairs originate from the malpighian layer or the stratum germinativum of the epidermis. Prenatal hairs are sometimes called lanugo and are either lightly pigmented or

contain no pigment. Prenatal or infant hair generally grows to a limit of about 15 cm see Table 1.1. It is very fine and by about 6–7 months after birth is replaced by slightly coarser hair, see Chap. 9 for details. Children's hair or primary terminal hair (pre-pubertal hair), is longer and coarser and generally grows to a length of about 60 cm. Primary terminal hair of children generally begins at about 2–3 years of age.

Soon after the onset of puberty, with its hormonal changes, hair fibers grow longer and coarser; producing what is called secondary terminal hair. In addition to these changes in scalp hair, hair in the axillaries, pubic, and beard areas (for males) becomes longer and coarser at the onset of puberty. Figure 1.10 shows that the maximum diameter of scalp hair for females peaks at a later age than for males (see Chap. 9 for details). The data of Table 1.1 shows that the time-span for anagen is shortest for infants, longer for children and longest from puberty to young adulthood. The data of this table also shows that the maximum attainable length and diameter for human scalp hair also correlate positively.

Table 1.1 Approximate human scalp hair length, diameter and anagen vs. age for female caucasians

Approximate		Approximate	
Hair type	Max. length (cm)	Diameter (μm)	Est. anagen (Year)
Infant	~15	30 (N = 26)[a]	~0.5
Children (0.9)	~60	62 (N = 82)[b]	~4 year
Adult (15.29)	~100	74 (N = 98)[b]	~6 year
Adult (30.89)	–	70 (N = 75)[b]	~5 year
Vellus	~0.1	~4	–

[a]Pecoraro V et al. [28], 26 full-term infants; hairs taken within 76 h of birth (13 males and 13 females). The average diameter of dark complexioned newborns was 37 μm while the average diameter for light colored hairs from light complexioned newborns was 22 μm
[b]Calculated from Bogaty [3] and from Trotter and Dawson [27]

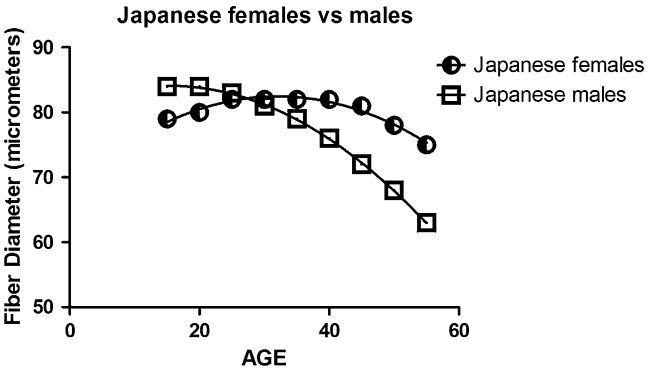

Fig. 1.10 Hair fiber diameter vs. age for males and females (see Chapter 2, section 2.3 "Aging influences on Hair" and Chapter 9 for details and references)

Table 1.2 Differences between primary-terminal and vellus hairs

Primary-terminal hairs	Vellus hairs
Long hairs (~1.0 m or longer)	Short hairs (~1 mm)
Thick hairs (30–120 μm diameter)	Thin hairs (4 μm or less)
Generally (not always) one hair per perpilosebaceous unit	More than one hair pilosebaceous unit
Usually pigmented	Non-pigmented
Longer life cycle (2–6 years in anagen)	Shorter life cycle (in telogen ~90% of time)

As one's age approaches maximum scalp diameter, hormonal changes induce slow gradual shortening of anagen for scalp hair of males. This action causes hair fibers to grow shorter and finer. Ultimately, in many persons this effect results in the transition of terminal hairs to vellus hairs, producing the condition commonly called baldness. Vellus hairs (Table 1.2) grow on those "hairless" regions of the body including the bald scalp, the nose, and many other areas of the body that appear hairless. Vellus hairs do not grow on the palms of the hands, the soles of the feet, the undersurface of the fingers and toes, the margin of the lips, the areolae of the nipples, the umbilicus, and the immediate vicinity of the urogenital and anal openings, the nail regions, and scar tissue.

The phrase, terminal hairs, is normally applied to those long thick hairs that occur during the latter stages of childhood and in adults. Terminal hairs, at some stage of development, grow on the scalp, eyelash area, eyebrow area, axillary and pubic areas, trunk and limbs of males and females, and the beard and mustache areas of males.

1.3.3 Extra Long Hair

As indicated, scalp hair at maturity normally grows to a length of about 3 ft (~90 cm); however, in long hair contests, lengths greater than 5 ft (~150 cm), see Fig. 1.9, are frequently observed and hair of several Guinness record holders have been measured at much longer lengths. Scalp hair length estimates by anatomical site, were made in Florida theme parks on 24,300 "adults" [29]. These hair length estimates by anatomical site were related to anatomical measurements to obtain estimates of free hanging hair lengths in centimeters. A plot of the natural logarithm of the percent population vs. these hair lengths provides a straight line and an equation that with several assumptions permits the estimation of the numbers of persons in the USA and the world with hair lengths up to 183 cm (just beyond ankle length) [30].

Data were also collected via a literature search for even longer hair lengths (ankle length or longer) to provide an equation to estimate the minimum numbers of

Table 1.3 Estimates of hair length in USA and global populations

% population (site)	Approximate Hair length (cm)	Approximate number of persons Calculated from equations A and B[a]
12.04 (Shoulder)	35.5	26.6 million in USA
1.88 (Shoulder blade)	55	4.2 million in USA
0.281 (Waist)	75	620,000 in USA
1.78×10^{-2} (Buttocks)	104	39,300 in USA
8.45×10^{-4} (Knees)	136	1,900 in USA
3.3×10^{-5} (Ankles)	170	73 in USA; 1,500 in world

[a]Numbers rounded off, except where fewer than 100

[b]Population of USA = 270 million, but since approximately 82% of the USA population are age 12 and above use 221 million as the adult population for the USA and since approximately 75% of the world's population are 12 and above use 4.5 billion as the adult population for the world

persons with exceptionally long hair [30]. Estimates of hair length from these studies are listed in Table 1.3.

In March of 1988, Dianne Witt of Massachusetts had the longest scalp hair on record (Guinness Book of Records). Her hair was measured at more than 10 ft long or more than 300 cm. Four years later it was measured at 12 ft (~366 cm) in length, so Ms Witt's hair appeared to be growing at a normal rate of about 6 in. per year (~15 cm). From this estimate of the growth rate at 15 cm/year and actual length, her hair has remained in anagen phase for more than 20 years, (see the section entitled, *A mechanism for hair growth/hair loss and changes in hair size*). So, it would appear that hair that grows to longer than normal lengths does not grow at an excessively fast rate; however it grows for longer time periods (longer anagen phase) than normal length hair.

1.3.4 Excessive Hair Growth

Hypertrichosis is a condition in which an excessive growth of terminal hair occurs usually on the limbs, trunk or face. Hypertrichosis may be localized or diffuse. The most common type is called essential hirsutism or idiopathic hypertrichosis of women. In this condition, terminal hairs grow on women in those areas where hairiness is considered a secondary sex characteristic of males, such as the trunk, the limbs, or the beard or mustache areas. This condition is generally not due to an endocrine abnormality, but is believed to be linked to the transport of testosterone from the endocrine glands to the site of activity (see Fig. 1.11).

Endocrinopathic hirsutism is a rare condition from excessive synthesis of hormones with androgenic properties. This abnormality produces masculinization of females. One symptom of this condition is excessive growth of terminal hairs in regions that are normally "hairless" in females. Classic examples of this disease are oftentimes exhibited in circus sideshows.

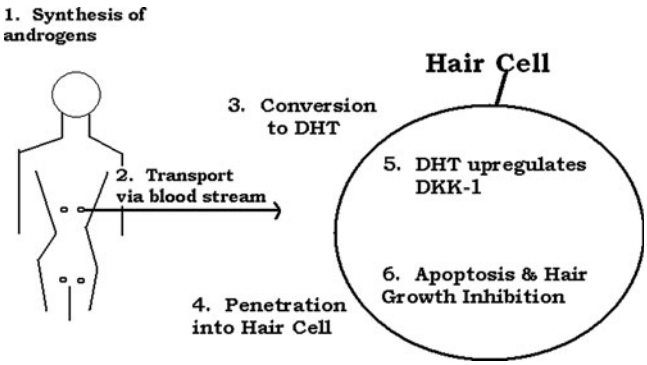

Fig. 1.11 Schematic illustrating how androgens combine with a protein receptor to form an active species that can either stimulate or inhibit hair growth

1.4 Hair Loss (Alopecia)

Hair loss actually involves the transition of terminal hairs to vellus hairs. This condition occurs gradually and at different rates for different persons. This section contains general information on hair loss both for men and women. Immediately following this section are detailed sections on male pattern alopecia and female pattern alopecia. Details and references on the chromosomes and genes involved in these alopecias are described in Chap. 3 in the section entitled *Some Other Hair Traits related to Genetics*.

The phenomenon of androgenetic alopecia tends to occur in a more diffuse pattern among women than men. The term "male pattern baldness" is used for the patterns of balding for men that either begin in the crown of the scalp and move forward or begin in the frontal area of the scalp and recede to create characteristic patterns (Fig. 1.12) which occurs in only a small percentage of women [6] as shown by Venning and Dawber [6].

1.4.1 Hair Density or the Number of Hairs/Unit Area

Barman et al. [31] suggested variation in scalp hair density (hairs/cm^2) between 150 and 300 among normal Caucasians, but current evidence shows this variation is more likely from about 75 to 450 terminal hairs/cm^2. Hair counts on normal scalps generally show less than 10% telogen hairs [32–34]. The considerable variation in hair counts occurs from the following variables: geo-racial group, age, method, scalp region and scalp conditions such as male and female pattern alopecia (later in this chapter) and the menopause (Chap. 2).

The hair density study summarized in Table 1.4 was carried out by Loussouarn et al. [35] on males and females from three different countries with more than 500

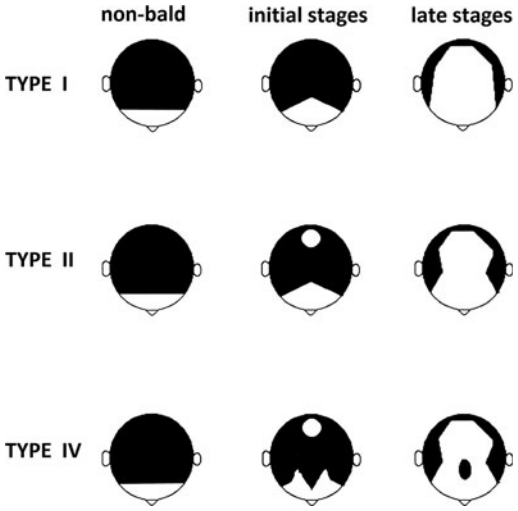

Fig. 1.12 Schematic illustrating different classes and types of male pattern alopecia. Various schemes have been described for classification of male pattern alopecia. This one was adapted from one of Hamilton's

Table 1.4 Comparative hair densities (hairs/cm^2) of different geo-racial groups (panelists 18–35 years of Age) [35]

	Hair density in terms of the number of hairs/cm^2 [a]					
	African (S. Africa + France)		Asian (Chinese)		Caucasian (Paris)	
	Female	Male	Female	Male	Female	Male
	N = 110	N = 106	N = 96	N = 92	N = 51	N = 56
Vertex	199 ± 42	188 ± 46	231 ± 37	217 ± 38	308 ± 68	264 ± 58
Temple	121 ± 38	128 ± 45	117 ± 19	122 ± 27	169 ± 35	151 ± 38
Occipital	167 ± 38	162 ± 41	182 ± 34	179 ± 30	250 ± 49	217 ± 37
Total mean	163 ± 51	160 ± 50	178 ± 57	173 ± 50	242 ± 77	211 ± 65

[a]Values are mean plus or minus standard deviations. Data shows a significant area effect but no significant difference between sexes. Both Asian and African groups provided significantly lower hair densities than for Caucasians

subjects between 1999 and 2003. The Asian subjects were Chinese recruited from Beijing (north China), Shanghai (Central China) and Guangzhou (South China). The Caucasians were from Paris or its suburbs and 98 Africans, living either in Johannesburg, South Africa plus 118 volunteers living in France, but native to West or Central Africa. To address a concern of the few Caucasian women in this study (51), I took hair density data from the parietal region of the scalp kindly provided by Dr Andrew Messenger (for "normal" Caucasian females who came to dermatology clinics with no concerns about hair loss) and analyzed the data for 102 subjects of age 18–35. Distribution analysis provided a normal distribution with a mean hair density of 290 ± 46 which is reasonably close to the hair density value by Loussouarn et al. for 51 female Caucasians of 308 ± 68 between the ages of 18 and 35 and provided reassurance to the data by Loussouarn et al. It also suggested that hair density of the vertex is similar to the parietal region.

This study by Loussouarn et al., with Chinese East Asians, Africans and Caucasians, is consistent with other studies showing that the hair density of Africans [32–34] and of Asians [36] is lower than that of Caucasians. Furthermore, from the data of Table 1.4 the hair density of Asians (vertex and occipital sites) appears to be slightly higher than that of Africans. The data of Table 1.4 suggests that the hair density of Chinese females ages 18–35 is about 25% lower in all three regions of the scalp than that of Caucasian females of the same age.

Loussouarn et al. also analyzed the hair density of males of these same geo-racial groups, see Table 1.4. The hair density of males by geo-racial group shows the same rank order as for females in all three scalp regions. Furthermore, the hair density in the vertex and occipital regions of males (ages 18–35) is significantly lower (matched pairs test) in all three geo-racial groups than for females of the same group. Loussouarn et al. explain this effect by "a difference which may be partially explained by the high prevalence of male androgenetic alopecia in this group".

These data (Table 1.4) also suggest approximately 81,000–121,000 hairs on the scalp (about 242 hairs/cm^2 times 500 cm^2 scalp area for female Caucasians = 121,000 scalp hairs; $178 \times 500 = 89{,}000$ scalp hairs for Asian females; and $163 \times 500 = 81{,}500$ scalp hairs for African females). It is frequently stated that humans lose about 100 hairs/day. For Caucasians assuming 121,000 hairs on the scalp and 7% of the hairs are in telogen phase which lasts about 90 days/year calculates to an average daily fall out of about 94 hairs. For Africans this would be about 63 hairs and for Asians about 69 hairs assuming hair counts as indicated by the data of Loussourarn et al. for females from ages 18 to 35 and the same percentage fall out for each of these three groups. This rate of hair shedding or fall out actually calculates to an average anagen period of about 3.5 years and we normally say it is about 2–6 years. So it is fair to say that adult female Caucasians ages 18–35 lose about 100 (94) hairs/day, Asians about 70 (69) and Africans about 60 (63) hairs/day.

Shedding rates, however, vary to a small degree seasonally and they normally decrease during and increase after pregnancy. Shedding rates also increase with age sometime in adulthood for females (in the mid to late twenties) and sooner for males (as shown later in this chapter). Lynfield [37] determined that the proportion of follicles in anagen increases during pregnancy. Additional details on the effects of pregnancy are described later in this chapter.

With regard to the seasonal effect, in a normal scalp the proportion of follicles in anagen peaks to nearly 90% in the spring (March in the Northern Hemisphere) in temperate climates and falls steadily to a low of about 80% in the late fall (November in the Northern Hemisphere) when the telogen count is highest as indicated by Randall and Ebling [38]. This effect is accompanied by increasing hair fall-out in the fall. As baldness approaches, the anagen time period decreases, thus the percentage of hairs in anagen (normally 80–90 plus percent) decrease as shown by Courtois et al. [39, 40]. The remainder of hairs is in catagen and telogen.

Anagen/telogen ratios are sometimes used as a criterion of the balding condition, that is, as balding progresses the ratio of anagen hairs to telogen hairs decreases. These ratios may be determined by plucking hairs and microscopically evaluating the roots (Figs. 1.13 and 1.14) or even better by the phototrichogram method

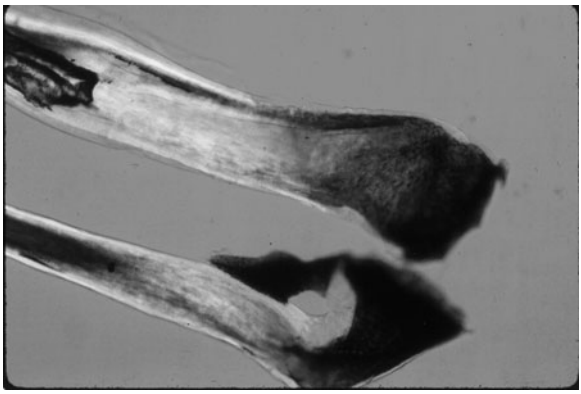

Fig. 1.13 A light micrograph of plucked hair fibers in the anagen stage

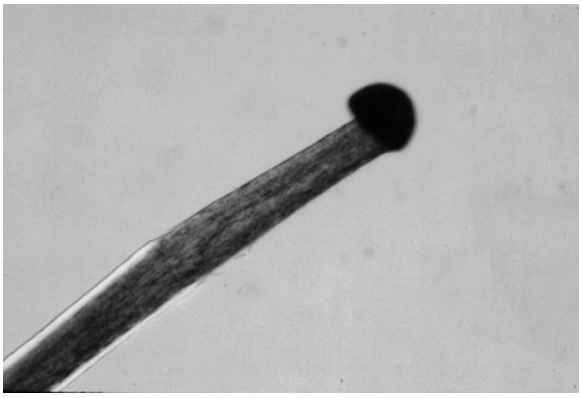

Fig. 1.14 A light micrograph of a plucked hair fiber in the telogen stage

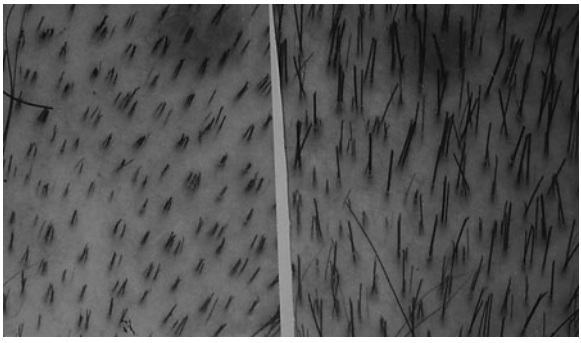

Fig. 1.15 Enlarged photographs of the scalp, *Left*: Immediately after shaving. *Right*: Three days after shaving. Grown hairs are in anagen and non-grown hairs in telogen

(Fig. 1.15) in which a small area of the scalp is shaved, photographed and re-photographed 3–5 days later. Comparison of the two photos reveals those hairs that have grown (anagen hairs, Fig. 1.13) and those hairs that have not grown (telogen hairs, Fig. 1.14) providing a determination of anagen/telogen ratios.

For additional details on hair density including hair density changes with age see the next sections on alopecia entitled *Male Pattern Baldness* and *Hair Loss Among Women*.

1.4.2 Male Pattern Baldness

Male pattern baldness or male pattern alopecia (MPA) is different from female pattern baldness in several ways such as in pattern (compare Fig. 1.12 with Fig. 1.16), incidence (70% of males vs. about 30% of females) and initial age (teens to early 20s for Caucasian males and the late 20s for Caucasian women (data suggests early to mid 20s). Norwood [41] described the incidence of MPA in 1,000 Caucasian males from ages 18 through the late 80s. He classified these males by the Hamilton-Norwood system a similar but more elaborate scheme than that depicted in Fig. 1.12. The data of Table 1.5 summarizes my analyses of these data.

Extrapolation of the data from the equation for Types III through VII (see Table 1.5 for definitions) suggests that Type III MPA begins in some Caucasian males as early as about age 16. The equation for Types III–VII incidence is $Y = -8.986 + 0.8689X.\ 0.01625(X-54.5)^2$ where Y = predicted incidence and X = age. I chose the linear over the quadratic model for types V–VII where: $Y = -10.09 + 0.5679X$ (Y = predicted incidence of types V–VII and X = age) because it was favored by p value and root mean square error. Averaging the extrapolations from the two different models suggests that type V MPA (see Table 1.5) begins in some persons as early as age 19 or 20.

The incidence of MPA Type III has been shown to be lower in both Korean (~14% in a study with 5,531 Korean men) [42] and Chinese men (~20% in a study with 3,519 Chinese men) [43] than in Caucasian men (~70%) [36], in agreement with the findings of Hamilton [44]. See Table 1.6 for additional comparisons at different ages.

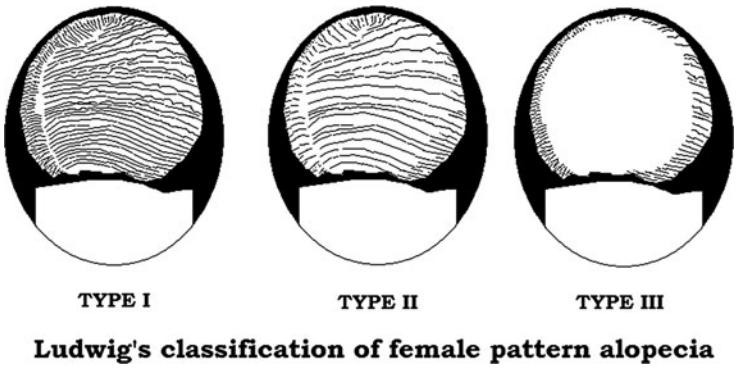

Fig. 1.16 Schematic illustrating Ludgwig's different types of female pattern alopecia

Table 1.5 Incidence of male pattern baldness from calculations of data by Norwood [41]

Age	% Types III–VII[a]	Predicted[b] % Types III–VII[a]	% Types V–VII[a]	Predicted[c] % V–VII[a]
20		7.0		1.3
24.5	12.4	15.7	4	3.8
30		25.3		6.9
34.5	37.6	32.5	9	9.5
40		40.3		12.6
44.5	46.7	46.0	14	15.2
50		52.1		18.3
54.5	53.8	56.3	20	20.9
60		60.6		24.0
64.5	64.4	63.4	31	26.5
70		65.9		29.7
74.5	64	67.2	32	32.2
80		67.9		35.3
84.5	70	67.8	36	37.9

[a]Type III is approximately Type I initial, Fig. 1.12; Type V is approximately initial Types II and IV and Type VII is late stages of Types II and IV of Fig. 1.12
[b]Quadratic model, $R^2 = 0.975$, Root Mean Square Error (RMSE) = 3.877 and $p = 0.0006$
[c]Linear model, $R^2 = 0.972$, RMSE = 2.279 and $p = 0.0001$

Table 1.6 Incidence of male pattern baldness in different geo-racial groups from prediction equations

Percentage showing any MPA Type III[a] through VII[a]				
Age	Caucasian[b]	Korean[c]	Chinese[d]	Asian estimate[e]
24.5	15.7	1.1	0.04	0.57
34.5	32.5	5.5	2.8	4.2
44.5	46.0	12.5	10.4	11.5
54.5	56.3	22.0	22.7	22.4
64.5	63.4	34.0	39.7	36.9
74.5	67.2	48.6	61.6	55.1

[a]Type III is Type I initial of Fig. 1.12 and Type VII is the late stages in Fig. 1.12
[b]From data of Norwood [41], Quadratic model $R^2 = 0.975$; $p = 0.0006$ (Equation above in text)
[c]From data of Paik et al. [42], Quadratic model $R^2 = 0.991$ and $p = 0.0009$
% MPA III–VII Korean = $-29.33 + 0.936\,\text{Age} + 0.01188(\text{Age}-49.5)^2$
[d]From data of Xu et al. [43], Quadratic model $R^2 = 0.993$ and $p = 0.0006$
% MPA III to VII Chinese = $-45.001 + 1.231\,\text{Age} + -0.02382(\text{Age}-49.5)^2$
[e]Average of Korean and Chinese data provides % MPA to represent Asian hair

Clearly MPA begins at an earlier age in Caucasian males than in Koreans or Chinese. Table 1.6 shows an average of the Korean plus Chinese data as an approximation for Asian men. Interestingly, only the last point at the highest age showed a large difference in these two Asian groups. The number for the Korean data point contained the least number of subjects 96 vs. 291 for the Chinese; therefore I would expect the data by Xu et al. for the Chinese subjects to be a more reliable representation of Asian hair for males. I have not been able to find similar extensive data for those of African descent. However, Setty [45] examined

300 Caucasian and 300 Black males at a hospital setting in Washington D.C. and indicated they were chosen randomly. Setty found a lower incidence of balding among Blacks vs. Caucasians.

1.4.2.1 Scalp Hair Density and MPA Versus Age

Among the many useful studies of scalp hair density in MPA was the one by Courtois et al. [40] who studied aging effects on hair cycles, including hair density and lengths of anagen along with an estimate of fiber diameters during an 8–14 year period on the same men (beginning at 25–32 years of age). These panelists are described in more detail in Table 1.7, along with hair densities measured by the phototrichogram method at the beginning and end of the program.

All three groups of subjects showed a reduction in hair density from the beginning to the end of the program with a larger reduction in hair density for the balding groups even though the hair densities were taken in the region of the scalp between the frontal area and crown, a region that is affected by MPA a few years after the frontal region and the crown. The author's described those areas as more prone to alopecia. For example, the frontal or crown areas, would show a more rapid decline in hair density over a shorter period of time. The non-balding group showed a 7.5% reduction in hair density while the 4 most balding members showed a 19.9% reduction in hair density and the 6 balding member group showed a reduction of 15.5% in hair density.

Courtois et al. [40] graphed their data over 3 year periods plotting the percentage of hairs with a growth period greater than X months for each individual on the abscissa vs. time in months (up to 36) on the ordinate. These curves confirmed that the ageing process of hairs in males (beginning at ages 25–32 over approximately a decade) shows a general decrease in the lifetime of hair fibers. This reduction in the lifespan of hairs at this stage of life for males was confirmed by analysis of variance.

Table 1.7 Hair density of men with and without MPA over an 8–14 year period [40]

Group	Hair density in number of hairs/cm^2 [a]			
	Beginning of program	End of program	Delta	Delta/10 years
Non-Balding[b]	288.5 ± 18.4	266.8 ± 12.8	21.7	16.7
Balding (all 6)[c]	219.7 ± 38.2	185.7 ± 21.1	34.0	36.0
Balding (4)[d]	235.8 ± 36.7	188.8 ± 26.1	47.0	49.6

[a]Hair density and telogen density were taken on the vertex, between the frontal area and the crown. This area is affected by MPA after the frontal region and the crown

[b]No signs of alopecia and with telogen density below 15

[c]Two of these subjects showed only fronto-temporal recession with grade III on the Hamilton scale and with telogen density approaching 20; the other four subjects are described below

[d]All four subjects showed more prominent frontal recession and thinning on the vertex than the two above and these four subjects showed grades III to V on the Hamilton scale. The proportion of hairs in telogen of these four subjects was approximately 30%

In addition, the finest hairs displayed the shortest anagen or growth periods, while the coarser hairs showed longer periods of growth.

Courtois et al. [40] pointed out that the average maximum length and the fiber diameters declined as the subjects aged. These scientists approximated hair diameters by comparing them with five groups of calibrated strings that were: very fine <35 μm; fine 35–50 μm; medium 51–65 μm; thick 66–80 μm and very thick >80 μm. Analysis of their data shows that the percentage hairs of the two coarsest diameter groups for each person of the balding group vs. non-balding group was significantly lower at both the beginning and the end of the test. In addition, the percentage difference from the beginning to the end of the test for the very fine diameter hairs of the balding subjects increased more than for the non-balding subjects to a significant degree ($p = 0.0006$). These results suggest that the reduction in fiber diameter with age for males likely appears over a few or several hair cycles and therefore could be different from females in FPA as concluded by Birch et al. [46].

1.4.3 Hair Loss Among Women

Female pattern alopecia (FPA) occurs as a diffuse reduction in hair density of the frontal and crown regions of the scalp; see the schematic of Fig. 1.16 depicting Ludwig's [47] original characterization of FPA. It usually begins just behind the frontal hairline, but in some cases the hairline can also decrease in hair density [48]. At one time it was believed that FPA and MPA were the same disease and both were due primarily to androgens [48]. However, several scientists including Norwood believe that these are two separate diseases. One reason is because the levels of incidence are different (MPA affects up to 70% of Caucasian males while FPA affects a little more than 30% of Caucasian women). In addition, MPA begins in the late teens (sometimes around age 16 for some males) to the early 20s when testosterone levels are high, while for female Caucasians, FPA begins in the twenties and peaks after about age 50 when testosterone levels are low. FPA and MPA also begin and occur in different regions of the scalp, compare Figs. 1.16 and 1.12.

1.4.3.1 The Incidence of Female Pattern Baldness among Caucasians Versus Asians

Norwood [48] determined the incidence of FPA in women by examining a total of 1,006 Caucasian women 20–89 years of age. Birch et al. [46] conducted an important study with two groups of women; one group consisted of 377 women, ages 18–99 that came to clinics for dermatologic reasons other than hair disorders. A second group of 47 women came to the clinic for reasons of hair thinning or FPA. These scientists ran several tests on both these groups of women including the

determination of FPA and hair density. I combined the incidence of FPA of the 377 women from the Birch, Messenger and Messenger study with the 1006 women from the Norwood study and determined best fitting equations. Predicted percentages of FPA from this model equation for the combined data of Norwood and Birch, Messenger and Messenger are summarized in Table 1.8.

By statistical analysis, the combined data of Norwood and Birch, Messenger and Messenger provides a better fit than the Norwood data alone. I believe that the predicted values for the incidence of FPA of Table 1.8 are the best data currently available for the incidence of FPA among Caucasians as a function of age. The incidence of FPA as a function of age of Tables 1.8 and 1.9, and the schematic of Fig. 1.16, define the incidence and region of the scalp that is most affected by this condition.

Table 1.8 Predicted incidence of female pattern hair-loss among Caucasian women from combined data of Norwood [48] and Birch et al. [46][a]

Age	Predicted % female pattern hair-loss
20	2.6
25	5.3
30	8.0
35	10.7
40	13.5
45	16.2
50	18.9
55	21.6
60	23.4
65	27.1
70	29.8
75	32.5

[a]The prediction equation was a linear model with an $R^2 = 0.948$ and $p = 0.001$, providing an equation of $Y = -8.32 + 0.545\ X$ where Y = the predicted incidence of FPA and X = age

Table 1.9 Incidence of FPA among Caucasian and Asian women

Age	Percentage with any female pattern baldness			
	Caucasian[a]	Korean[b]	Chinese[c]	Ave. Korean + Chinese[d]
24.5	3.3 (4.8)	0.2	0	0.1
34.5	14.8 (11.2)	2.3	0.3	1.3
44.5	13.5 (15.8)	3.8	0.8	2.3
54.5	20.8 (20.8)	7.4	1.7	4.6
64.5	26.6 (32.9)	11.7	3.3	7.5
74.5	33.1 (32.9)	24.7	15.4	20.1

[a]Combined data of Norwood [48] and Birch et al. [46] in parentheses from prediction equation $Y = -8.32 + 0.545X$, where Y = incidence of hair loss and X = Age
[b]Data of Paik et al. [42]
[c]Data by Xu et al. [43]
[d]Average of Korean and Chinese hair represents the incidence for Asian hair [42, 43]

1.4.3.2 Incidence of FPA Among Caucasians Versus Asians

The incidence of FPA or extensive hair loss among Asian women is lower than among Caucasian women. For example, Paik et al. [42] studied hair loss in Korean men (5,531) and women (4,601) and found 24.7% of women over 70 years of age have FPA. This value of 24.7% FPA among Korean women that are more than 70 years of age can be compared with 33% among Caucasian women and 15.4% among Chinese women by Xu et al. [24].

Xu et al. [43] studied the incidence of hair loss in Chinese women in Shanghai, China and found a numerically lower incidence of hair loss at all ages than for the study among Korean women, see the data of Table 1.9. The hair loss from these two groups of Asian women is clearly lower at all ages than for the Caucasian women, see Table 1.9. The data was also combined for the Korean and Chinese women providing average values used as estimates for Asian women. Ludwig Type I hair loss was the most common up to the sixth decade for the Korean women. In the sixth decade and at higher ages Ludwig types I and II showed similar occurrence.

1.4.3.3 Hair Density of Men Versus Women and Children Versus Adults

The paper by Birch et al. [46] together with papers by Pecoraro [28, 49, 50] and by Loussouarn et al. [32, 35] provides an entry into hair density as a function of age among women. Only relatively small studies (generally at age 35 or less) were found comparing hair density of men vs. women who were not affected by alopecia. In those cases there were no significant differences in hair density among men vs. women. The study by Loussourarn et al. [35] summarized by Table 1.4 shows lower hair densities for males than females. These scientists attribute part of that difference to male androgenetic alopecia. If differences do exist in hair density between men and women with no signs of androgenetic alopecia, they must be either small and or region or age specific.

Pecoraro, Astore and Barman provide an indication of hair density of children before puberty [49] vs. adults [50] in two of their papers. In their paper on adults from ages 16 through 46 (with only 17 males and 22 females), these scientists found a wide range in hair densities from 175 to more than 300 hairs/cm^2 while Birch et al. [46] found an even wider range from just over 75 to nearly 450 hairs/cm^2 for more than 300 females.

Pecoraro et al. also estimated hair coarseness using 3 coarseness groups: thick (~100 μm), medium (~50 μm) and fine (~25 μm) and noted a decrease in coarseness of hair over the entire scalp, in both sexes, as age advances peaking between ages 16 through age 33 and declining from age group 24–33 to the higher age groups. They also noted that the percentage of telogen hairs increased in all scalp regions with increasing age with the largest change occurring in the coronal region. Note, Pecoraro et al. did not examine the temporal region of the scalp. These scientists also noted decreasing hair density especially in the coronal region with increasing

Table 1.10 Comparative hair densities of children vs. adults in different scalp sites

Region of scalp	Children (ages 3–9) [49]	Adults (ages 16–46) [50]
Crown or coronal	233 highest density	202 lowest density
Parietal	170 lowest density	232 high density
Frontal	196	212
Occipital	193	236 highest density

Table 1.11 Data from quadratic models of "normal" subjects vs. subjects with self perceived hair loss [51]

	Predicted hairs per cm^2 by quadratic model		Instantaneous rates	
Age	"Normal" (N = 315)	Self perceived loss (N = 1,099)	"Normal"	Self perceived loss
25	291.7	272.4	−0.86	−0.65
30	286.9	268.0	−1.05	−1.10
35	281.2	261.4	−1.23	−1.56
40	274.6	252.5	−1.42	−2.01
45	267.0	241.3	−1.61	−2.47
50	258.5	227.8	−1.79	−2.92
55	249.1	212.1	−1.98	−3.38
60	238.8	194.1	−2.17	−3.83
65	227.4	173.8	−2.36	−4.29

age, consistent with data of Birch, Messenger and Messenger. Table 1.10 compares hair densities of pre-pubertal children with those of adults. The hair densities for adults of Table 1.10 appear on the low side (compared with the data of Table 1.11); hopefully the relative differences within the study by Pecoraro et al. are more meaningful. Note the different distribution of hair density on the different scalp regions of the children vs. the adults.

As the data of Table 1.10 show, the children display the highest hair density in the crown or coronal region of the scalp. In direct contrast, adults show the crown to contain the lowest hair density while the occipital and parietal regions contain the highest hair counts. But, the parietal regions contain the lowest hair density of these scalp regions in children. Might this effect in the coronal region vs. the other regions be a sign that the condition of baldness is already beginning because the crown or coronal region of the scalp which has the highest hair density before puberty becomes the lowest hair density after puberty and is the region or part of the region most affected by MPA and possibly by FPA.

1.4.3.4 Hair Density Versus Age for Caucasian Women

Hair densities vs. age in the parietal region of the scalp have been compared for two groups of Caucasian female panelists, one group by Birch et al. [46] and another by Robbins et al. [51]. Both data sets show a highly significant fit for quadratic and cubic models for hair density vs. age with a maximum in hair density in the mid to

high twenties age range. A plot of the data by Robbins and Dawson et al. is summarized in Fig. 1.17. For this study, the site was the left and right parietal region about 3.8 cm from the vertex on each side of the scalp toward the tip of the ear for 1021 Caucasian women from age 18 to 66 (providing more than 2,000 data points). These women believed they had some hair loss. For this figure the data were condensed to 95 data points by ANOVA and then regressed vs. age.

Birch et al. [46] determined hair densities on another group of Caucasian females consisting of more than 300 women age 17–86 who came to dermatology clinics with no complaints about baldness. The site in which hair density was determined was "within a 1 cm diameter circle, about 2 cm lateral to the midline of the scalp, halfway between the vertex and the frontal hair line" in the parietal region of the scalp. Note, the primary difference in the subjects of these two groups of Caucasian women was that the Birch, Messenger subjects came to dermatology clinics with no complaints of hair loss whereas the Robbins and Dawson et al. [51] subjects were enrolled because they perceived hair loss themselves. Therefore the Birch, Messenger group could be called the "normal" or control group.

Best fitting quadratic models were calculated and data from both groups of these panelists are summarized in Table 1.11. These data confirm the findings of others that there is a gradual decrease in hair density with age from near the mid-twenties for female Caucasians which has been shown for other races. Table 1.11 also contains instantaneous rates of hair loss at different ages for the women with self perceived hair loss and those with no complaints of hair loss. These rates were obtained from the first derivatives of the quadratic equations from the regression models and show gradual increases in the rates of hair loss with increasing age. At age 30 and above the differences in these instantaneous rates of hair loss for these two types of panelists become increasingly larger.

This latter effect is illustrated by the rates of change of the rates of hair loss (analogous to acceleration constants) calculated from the second derivatives of the quadratic regression models summarized in Table 1.12 and demonstrates that the instantaneous rates of hair loss from the panelists with self perceived hair loss are increasing at a faster rate than the "normal" panelists.

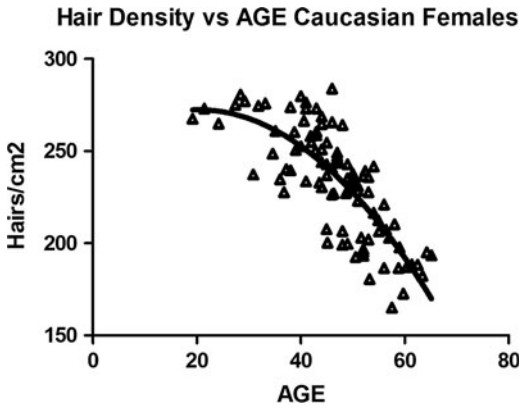

Fig. 1.17 Hair density (hairs/cm^2) vs. age for Caucasian females; in the parietal region of the scalp [51]

Table 1.12 Comparative rates of change of the rates of hair loss of normal subjects vs. those with self perceived hair loss [51]

	"Normal" subjects	Self perceived hair loss subjects
Rate of increase of rates of hair loss	0.038	0.091

Birch, Messenger and Messenger also noted that subjects with high hair density 350 or greater tended to display multiple hairs emerging from single follicles, while those with low hair densities generally less than 200 usually had single hairs rising from most follicle orifices. Others have cited a similar finding [52]. The effects of menopause on hair density and diameters are described in Chap. 2 in the section entitled, *The Effects of Menopause on the Lipids in Hair and on the Hair Fiber*.

Hair loss was studied among Japanese women by Tajima et al. [52] and others [53, 54]. These scientists examined 159 women (46 suffering from hair loss and 113 with little to no hair loss) showing similar effects to the data of Birch, Messenger and Messenger, that is a decrease in hair density with increasing age beyond the mid-twenties. The hair density with respect to age for these Japanese women were slightly lower (5–20% in the different age groups), but otherwise similar to those of Birch, Messenger and Messenger among the Caucasian women.

1.4.3.5 Factors Involved in the Perception of Female Pattern Baldness

Birch, Messenger and Messenger state in this paper [46] that the perception of hair loss is generally determined primarily by decreasing hair density. However, these scientists add that for initial discrimination between Ludwig type I hair loss (Fig. 1.16) and no hair loss, larger hair diameters could weaken discrimination. Another way of saying this is that the subjective impression of FPA is multi-factorial involving hair density, hair fiber diameter and very likely hair fiber curl or the degree of curliness and possibly other factors. The work of Robbins and Dawson et al. [51] support this proposal by demonstrating that both hair density and diameter contribute to the perception of the relative hair amount in a new metric called "relative hair coverage" described in detail in Chap. 10.

Supporting the conclusion that hair curvature should be considered in determining the perception of hair baldness are the facts that increasing hair curvature increases hair volume or body and several small studies show that curly African hair and African American hair has fewer follicles and fewer hairs/cm^2 [32, 33, 35] as compared to Caucasian adult hair and yet the coverage on non-alopecia scalps appears to be at least equivalent.

For women who suffer hair loss such that their hair density is on the low side (150–200 hairs/cm^2), but close to the spectrum of the normal distribution of hair density, other factors such as hair fiber diameter and the degree of curliness will likely enter into their subjective interpretation of FPA. A 25–30% hair density decrease from 400 hairs/cm^2 might be detectable for fine straight hair even though the hair density would still appear rather high at nearly 300 hairs/cm^2. To illustrate

this point, Birch, Messenger and Messenger found a wide range of hair density in subjects who were not concerned with FPA, ranging from approximately 75 to nearly 450 hairs/cm^2. In this study, the clinicians classified more than 50 women (about 15%), among this group not concerned with FPA, as having FPA. The median hair density of that group with FPA was approximately 188 hairs/cm^2, while the median for those not classified as having FPA was approximately 263 hairs/cm^2. Birch et al. [46] also classified three women with a little more than 300 hairs/cm^2 as having FPA. Now, if these high hair density women had very fine and straight hair and they had undergone nearly 30% hair loss from about 430 to 300 hairs/cm^2 then they would likely have been classified clinically as having FPA.

1.4.3.6 Normal or Acceptable Hair Loss

So, what is "normal" hair loss that is acceptable to women? The data of Table 1.11 along with the work of Birch et al. suggests that some women can suffer as much as 25–37% hair loss or decrease in hair density without complaining about hair loss. So, I conclude that a hair density decrease of 30 $\pm$ 5% in the top central area of the scalp just behind the frontal hairline, would be the borderline hair loss at which the factors of hair fiber diameter and hair fiber curl become more and more important with regard to the self determination or perception of a problem with hair loss among women. If the hair is fine and straight then a hair density decrease less than 30% will likely cause concern.

Interestingly, another group of women that Birch, Messenger and Messenger studied was a group of women who came to the clinic with hair loss as their major complaint. The most severe hair loss among this group had hair density less than 125 hairs/cm^2. Assuming a starting point at 290 hairs/cm^2 would provide a hair density decrease of 57%. So clearly a hair density decrease of more than 50% should provide a real hair loss problem for most women regardless of fiber diameter or degree of curl.

1.4.3.7 Hair Miniaturization or Diameter Change in Females Versus Males

Birch et al. [46] examined hair fiber diameter changes and found an extremely weak correlation between hair fiber diameter changes and hair density, $R^2 < 0.03$. This conclusion is consistent with the fact that maximum diameter for women occurs in the early to mid-forties [51] and then decreases with advancing age as most of the literature suggests, see Chap. 9 for additional details. On the other hand, maximum hair density occurs in the mid-to-late-twenties [51].

Birch et al. [46] concluded that if hair miniaturization does occur in FPA it must be different from the balding process in men. Moreover, they suggested that the miniaturization of hairs likely occurs rapidly inside a single hair cycle or over a few years in FPA as opposed to a lengthy gradual process over several hair cycles for

MPA. I could find no confirmation of this suggestion in the literature. Nevertheless, this is an interesting observation that needs to be re-examined, because if it is correct it is very important.

1.4.4 Pregnancy and its Effects on Scalp Hair

One of the clearest non-technical summaries of what happens during pregnancy can be found in the following website of the Mayo Clinic at mayoclinic.com: This website explains that hormone levels during pregnancy inhibit normal hair loss on the scalp. Therefore, during pregnancy one usually observes a "lush head of hair". But, after delivery, the excess hair is shed in a very short timeframe. This effect often provides a shock to the postpartum mother. But, usually within 6 months the hair returns to normal.

As indicated, the mechanism for hair growth involves three stages: A growing period called anagen; a transition period, catagen and a resting period, telogen. At telogen, the "old" hair falls out and is replaced by a "new" hair fiber. The time-span of anagen is normally 2–6 years which determines how coarse and how long scalp hair fibers become. The time-span of anagen is shortest for infants, longer for children and longest from puberty to young adulthood (~ages 13–30). Then sometime in the adult stage of life, anagen becomes shorter with further advancing age, earlier for men (late teens to 20) than for women (mid-to-late-twenties). The percentage of hairs in anagen is normally 85–90% and most of the other hairs are in telogen. The lower the percentage of anagen hairs means more hair fall out and usually signifies alopecia.

Lynfield [37] was the first to provide a general understanding of what happens to scalp hair during and after pregnancy. Lynfield concluded, contrary to the existing view in 1960, that the time of onset and the length of time that hair loss occurs postpartum are highly variable. Lynfield determined that the period of anagen is longer than normal during pregnancy; therefore there is less fallout during that time. However, after delivery there is usually a larger amount of hair loss than normal.

Lynfield [37] began her study with 26 Caucasian women (ages 17–38) and examined the hair roots of different numbers of these women during and after normal pregnancies. She compared her data with a control group of 30 healthy non-pregnant women ranging from age 17 to 40. Lynfield determined anagen and telogen counts by examining hair roots of 50 hairs at a time, in both the frontal and temporal scalp. She focused her results primarily on temple hair since the temporal data provided less experimental scatter, but she indicated that the changes were parallel in both regions of the scalp.

Lynfield's [37] data showed normal anagen percentages, near 85%, in the first trimester of pregnancy for five subjects. These percentages compared favorably with the mean anagen hairs in the non-pregnant control group at $85 \pm 5.6\%$ (mean $\pm$ standard deviation). During the second and third trimester and the first week postpartum, the anagen levels rose to 95%, 94% and 94% respectively.

However, in the sixth week postpartum the anagen levels dropped to 76% and 77% and in the few cases examined at a later time (not specified, but 5 and 8 months from the graph of one subject) the anagen density generally returned to normal. Lynfield noted that contrary to the existing view in 1960, her data indicated that the time of onset and the length of time that hair loss occurs postpartum are highly variable. The time of onset began almost immediately after delivery in two women, 1 month postpartum in 1 and 4 months postpartum in another and it lasted up to 5 months.

Lynfield [37] described one clear exception as a 38 year old woman in her seventh pregnancy whose anagen levels were essentially unchanged and no clinical hair loss was detected. Lynfield speculated that after several pregnancies the hair roots of this woman did not respond to "hormonal fluctuations of pregnancy". She also described five other women whose anagen counts decreased postpartum, but no hair loss could be detected by the clinicians. So, not only are the times of onset and the length of hair loss postpartum highly variable, but the clinical detection of hair loss postpartum is also highly variable.

Pecoraro et al. [55] reported an increase in the proportions of thick to medium and thin hairs during pregnancy. Nissimov and Elchalal [56] confirmed this finding and identified that the mean major-axis diameter of scalp hair was higher in 12 pregnant vs. 13 non-pregnant women. The major-axis diameters of the pregnant women increased (+4.5%), and this increase was first detected at about 2 weeks after conception through the 35th week of pregnancy. On the other hand, the major-axis diameters of the non-pregnant women decreased (−5.2%) toward the scalp over the same 35 week period. This difference is statistically significant at a high level of confidence.

About a little more than a decade ago, Hutchinson and Thompson [57] reported changes in the major-axis diameter of human scalp hairs that they associated with changes occurring inside the follicle. They concluded that hair fibers are not uniform cylinders, but from the distal end toward the scalp there is an increase in size over about a 6–8 cm length (about 3 weeks growth) of fiber, that they associated with the start up of anagen. After that distance the major-axis of the hair fiber decreased progressively through anagen. These effects were confirmed by the work of Nissimov and Elchalal [56]. See the section on hair fiber ellipticity in Chap. 9 for additional discussion on the effect of diameter and ellipticity changes on single hairs over time.

The only data I could find on growth rates during pregnancy are by Pecoraro et al. [55] which indicated 0.0325 cm/day in the first trimester, 0.0315 cm/day in the second trimester and 0.0329 cm/day in the third trimester. Comparing these data with Pecoraro's [50] data in an earlier publication shows adult scalp hair of females grows at 0.0344 cm/day. This suggests that the growth rate slows down during pregnancy. This growth rate effect, if real, could relate to the body compensating for the increased protein demand and number of hair cells required by thicker hair fibers produced during pregnancy and the increase in the number of anagen hair fibers.

The thorough review paper by Ohnemus et al. [58] describes the hair follicle as a target for estrogen, but cautiously states that because of the complex associated

endocrine changes during and after pregnancy it is still not clear whether estrogens or other hormones initiate these effects on hair fibers during and after pregnancy. Also, more data with larger numbers of subjects on hair density of males and females of different geo-racial groups vs. age would be helpful for predicting effects of important cosmetic hair properties and treatments vs. age.

1.4.5 Alopecia Areata, Universalis and Other Forms of Hair Loss

Alopecia areata, another form of hair loss, is believed to be related to the immune system (e.g., autoimmunity). This disease generally occurs as patchy baldness on an otherwise normal scalp, although sometimes hair of other body regions is affected. When the entire scalp is involved, the condition is called alopecia totalis. If terminal hair loss occurs over the entire body, a rare condition, it is called alopecia universalis. Emotional stress has been shown to be one of the initiating causes of areata. See the section in Chap. 7 entitled, *Sudden Graying-whitening of Hair* where alopecia areata has been suggested to be involved. Topical application of steroids is sometimes used to treat areata. However, even when untreated the balding area in time often returns to normal hair growth.

Alopecia induced by physical stress has been termed trichotillomania. This condition occurs from physically pulling or twisting a localized area of hair until noticeable thinning develops. This type of hair loss sometimes occurs in children who unconsciously pull or twist a group of hairs. A similar type of hair loss also occurs in adults.

Telogen effluvium is a term used to describe a sudden but diffuse hair loss that is often caused by an acute physical or psychological stress. This condition usually lasts only a few months and is often reversible. Telogen effluvium has been associated with dandruff and its treatment is described in Chap. 6 in the section on dandruff.

Drugs used in chemotherapy often induce alopecia. However, this type of hair loss is also usually reversible and the "new hair" after chemotherapy can be of a different curvature or a different color than the hair prior to chemical treatment.

1.5 A Mechanism for Hair Growth/Hair Loss and Change in Hair Size

The ratio of anagen to telogen hairs indicates whether hair growth or hair loss is occurring. The length of anagen activity controls the changes in hair size that occur during different stages of the life of mammals. At different ages of humans, such as shortly after birth, at puberty or at maturity, hairs grow to different sizes (different

lengths and diameters). All of these changes generally involve hormones or chemical messengers. See the section in Chap. 2 entitled *Aging Influences on Hair* and the previous section on *Hair Growth* in this Chapter.

Loussouarn et al. [35] described hair growth rates of scalp hair for three different geo-racial groups in these three scalp regions (vertex, temple and occipital). This study showed that the growth rate of the hair of East Asians is higher than that of either Caucasians or Africans, see Table 1.13. The growth rates of the scalp hair for females of these three geo-racial groups' shows that the scalp hair of Africans grows slower than the scalp hair for either Caucasian or Asian females. Furthermore, the growth rate of the scalp hair of Asian females is slightly higher than that of Caucasian females.

The growth rates of males of these same geo-racial groups is summarized in Table 1.13 and parallels the growth rates for females showing slower rates for Africans in all three scalp regions and slightly higher growth rates for Asians than Caucasians.

Over the past five decades, many ingredients have been demonstrated to either inhibit or to promote hair growth, see Table 1.14. More than 40 years ago, Hamilton [59] demonstrated that androgens are a factor in male pattern baldness. For example, long-term injections of testosterone induced a rapid transformation of terminal hairs to vellus hairs in the frontal scalp of stump-tailed macaques [59, 60]. Thus, testosterone, an androgen, produced by the adrenals and the sex glands was shown to play a critical role in controlling the growth patterns of human scalp hair fibers.

Estrogen, a generic term for any substance that exerts biological effects as hormones like estradiol, have been shown to produce positive effects on hair growth when taken internally or applied topically. Systemic estrogen probably prolongs the anagen phase of hair growth by suppressing androgen production [60], and both estrogens and anti-androgens when applied topically have been shown to be capable of suppressing hair loss as shown by Schumacher-Stock [61]. Anti-androgens, substances that are capable of blocking androgen function, include spironolactone, cyproterone acetate, progesterone, finasteride (Fig. 1.18) and dutasteride. These last two ingredients of Table 1.14 are inhibitors of 5-alpha-reductase an important

Table 1.13 Rates of growth of hair of different geo-racial groups (all panelists 18–35 years of age) [35]

	Growth rate in terms of micrometers/day[a]					
	African		Asian (China)		Caucasian	
	Female	Male	Female	Male	Female	Male
	N = 110	N = 106	N = 96	N = 92	N = 51	N = 56
Vertex	294 ± 49	282 ± 52	413 ± 51	430 ± 55	379 ± 51	364 ± 66
Temple	282 ± 46	286 ± 50	393 ± 55	406 ± 46	357 ± 53	368 ± 57
Occipital	274 ± 59	258 ± 48	410 ± 54	417 ± 50	364 ± 56	371 ± 53
Total mean	284 ± 49	275 ± 51	405 ± 54	418 ± 51	366 ± 54	368 ± 58

[a]Values are mean plus or minus standard deviations. Data shows a significant area effect but no significant difference between sexes. These data show that the growth rate for Asian hair is significantly higher than for either Caucasian or African hair

Table 1.14 Some ingredients known to affect hair growth

Retard hair growth	Promote hair growth
Testosterone	Streptomycin
Dihydrotestosterone	Cyclosporin
Retinoids	Diazoxide
Retinoic acid	Estrogens
Retinol	Estradiol
Eflornithine[a]	Progesterone
	Spironolactone
	Minoxidil[b]
	Finasteride[c]
	Dutasteride[c]

Molecular signals essential to follicle induction and growth such as BMP's, sonic hedgehog, several WNT proteins and several receptors such as BMPRIA EGFR, EGRF and TGFR were not included in this table

[a]Chemotherapy drug (known to inhibit polyamine biosynthesis and ornithine decarboxylase)

[b]Potassium channel opener and vasodilator

[c]Inhibits 5-alpha-reductase (conversion of testosterone to dihydrotestosterone)

enzyme in the conversion of androgens to the most active form of testosterone. The topical application of estrogens and anti-androgens probably cause a local inhibition of the androgen function and demonstrate one solution to hair growth, as shown by the proposed mechanism below.

Chemical cures for baldness and the search for a better understanding of the mechanism of this phenomenon often involve androgens, genetic studies and drugs known to be capable of inducing hypertrichosis, such as streptomycin, cyclosporin, diazoxide, tacrolimus (fujimycin), estradiol, oxandrolone, minoxidil, finasteride and dutasteride. Several of these drugs have shown promise in reversing the symptoms of male pattern baldness. Minoxidil and finasteride are currently sold as active ingredients in hair growth products.

Minoxidil (6-amino-1, 2-dihydro-1-hydroxy-imino-4-piperidino pyrimidine) has been shown to re-grow hair with minimal side effects. This drug is a vasodilator and a potassium channel opener. It was originally developed by Upjohn for treatment of hypertension, and has been shown to be capable of reversing male pattern alopecia in clinical trials during treatment periods. However, with minoxidil, best results are obtained under occlusion and in subjects whose condition of balding has not progressed for many years. The re-growth is concentration dependent with a higher efficacy at 5% than 2% active ingredient. Minoxidil is currently sold as a topically applied drug under the trade name Rogaine.

Finasteride (see Fig. 1.18) a drug developed by Merck & Co. for treatment of benign prostate hypertrophy has been shown to inhibit the enzyme 5-alpha-reductase, and thus, to block the conversion of testosterone to the more active 5-alpha-dihydrotestosterone (DHT) [62, 63]. There are two forms of the enzyme 5-alpha-reductase, called Type I and Type II. Finasteride is capable of blocking only the Type II enzyme which is the predominate form of this enzyme in the hair

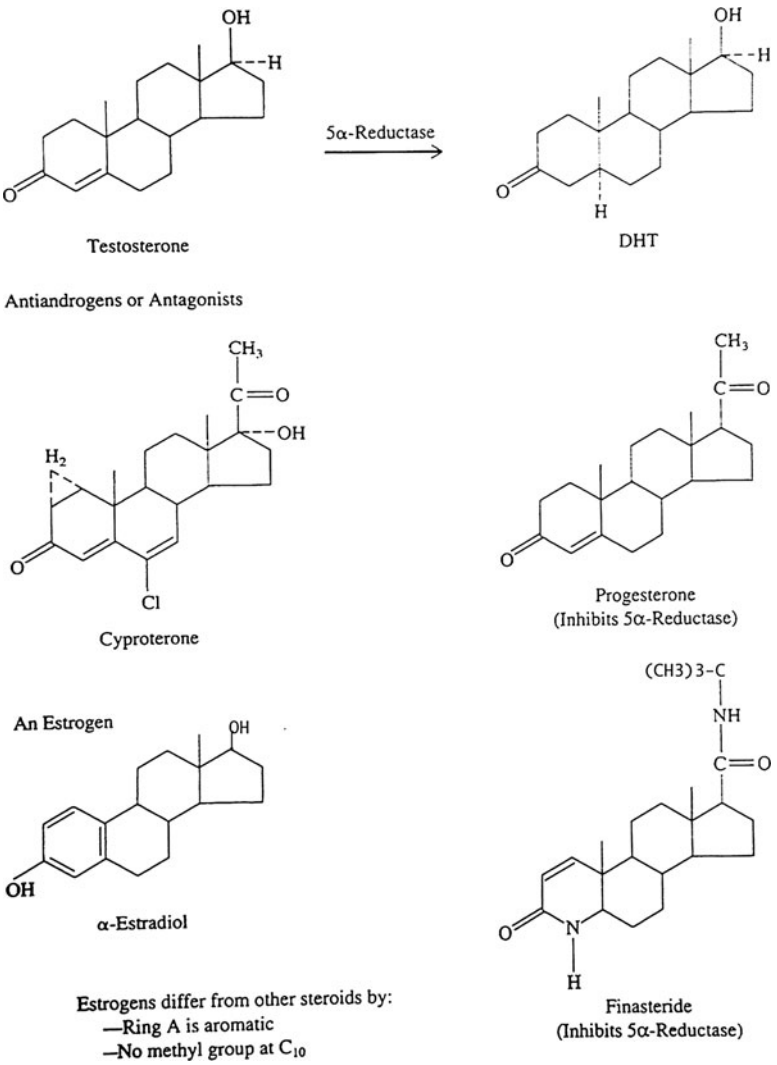

Fig. 1.18 Chemical structures of the active androgens, testosterone and dihydrotestosterone (*DHT*), some examples of antiandrogens, an estrogen and finasteride

follicles and the prostate gland. This action in hair follicles (partially blocks the conversion of testosterone to DHT) suppresses the androgen inhibition of hair synthesis in the hair follicle, thus extending the anagen period to provide longer and coarser hairs [64, 65]. Sung et al. [66] provided evidence that DHT up-regulates DKK-1 from dermal papilla cells thus causing apoptosis in keratinocytes and inhibits hair growth.

Propecia is the trade name for the hair treatment form of finasteride, sold in pill form and taken orally. It is recommended only for males because of potential

problems during pregnancy. Dutasteride (Avodart, a drug for benign prostate hyperplasia) from Glaxo has been touted as an effective hair growth agent that works similar to finasteride, but it has a longer half life (longer residence time in the body), is more active in inhibiting 5-alpha-reductase and more importantly it inhibits both Type I and Type II forms of the enzyme 5-alpha-reductase. Dutasteride is more effective in lowering DHT levels and appears to work faster in the treatment of baldness than finasteride. However, as of this writing the data is not clear that it is a more effective treatment for androgenetic alopecia.

Normal control of the anagen/telogen cycle by the action of androgens (such as the action of 5-alpha-reductase on testosterone), or by anti-androgens and the subsequent alteration of hairs to different sizes is summarized below, also see Fig. 1.11: Molecular signals (Wnt proteins and Sonic hedgehog) most likely from mesenchymal cells called dermal condensate are transported to stem cells in the bulge (Fig. 1.5) to initiate lower follicle formation and anagen [11–22, 67].

Oshima et al. [68] described that stem cells in the bulge move downward in the follicle and divide rapidly to form the follicle matrix. The follicle matrix then begins producing inner and outer root sheath cells and ultimately cuticle, cortex and medullary cells along with the other essential proteins and structures in the lower follicle, see Fig. 1.6.

Cell division continues at a rapid rate and differentiation occurs as the hair shaft cells move upward in the follicle. During various stages of growth, signaling molecules and metabolites are transported between the different cellular layers of Fig. 1.6 to the sites where they exert their activity.

The synthesis or the production of androgens by the adrenals and the ovaries or the testes occurs. These androgenic hormones are transported in the blood stream on carrier proteins such as sex hormone binding globulin (SHBG), to peripheral tissues such as the pilosebaceous apparatus. These hormones then dissociate from the binding proteins.

Testosterone is converted in the hair follicle to the more active hormone DHT.

Testosterone and DHT are transported into hair cells. These steroids act inside the keratinocytes to induce apoptosis most likely involving a receptor protein.

Thus, any agent or process that either enhances or interferes with any of these steps will lead to either greater or less production of longer more coarse hairs. Interference in the transport of androgenic hormones in the blood stream may result in terminal hairs being produced where vellus hairs are normally produced. For example, Barth [69] has shown that the step involving the transport of testosterone on carrier proteins occurs in hirsute women. This effect leads to a reduction in transport proteins (SHBG) and the concomitant increase in the free unbound testosterone level in the blood stream. Thus, the transport mechanism is interfered with and thick terminal hairs are produced in body regions where they are not normally produced.

Not only is the transport of testosterone important, transport of other androgens capable of being synthesized into testosterone is also important, because Sawaya et al. [70] demonsrated that the enzyme 3-beta-hydroxysteroid dehydrogenase which converts other androgens into testosterone (see Fig. 1.19) shows greater

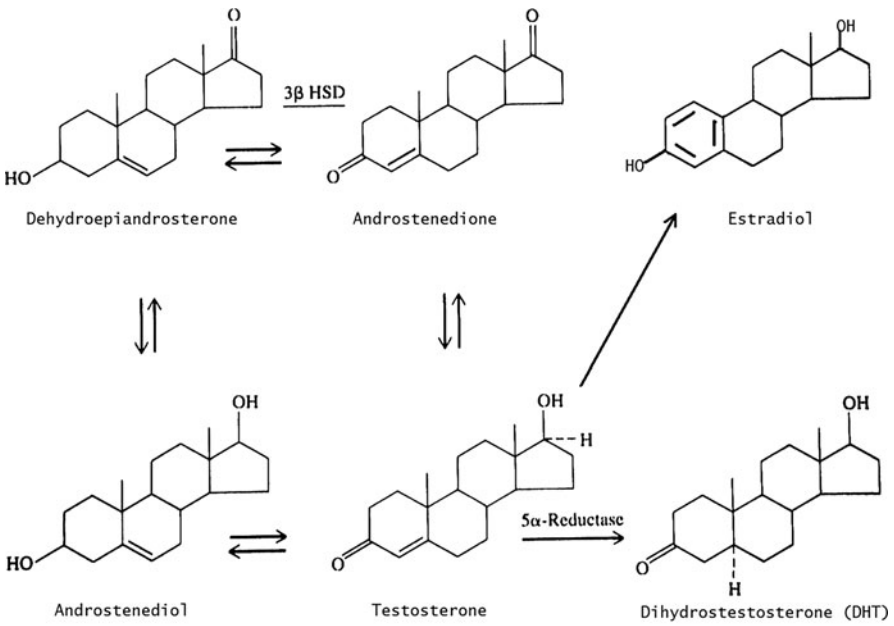

Fig. 1.19 The conversion of androgens to testosterone and DHT

activity in samples of balding scalp as compared to normal hairy scalp. In addition, balding men show increased activity of the enzyme 5-alpha-reductase in the pilosebaceous units and in the skin of the frontal scalp. On the other hand, Griffin et al. [71] concluded that men with a deficiency of this enzyme do not develop baldness. Also see the section entitled *Gene Therapy for Potential Treatments for Hair Loss* later in this chapter.

As indicated, androgens including testosterone are produced by the testes and the adrenal glands [72] and then transported to the sites of activity. Hair root cells contain androgen receptors; however, there is evidence that these receptors are intra-nuclear rather than intracellular, see King and Greene [73] and Welshons et al. [74]. In addition, Sawaya et al. [75] demonstrated a greater androgen binding capacity (DHT) in the nuclei of sebaceous glands taken from patients with bald scalps than from patients with normal hairy scalps. Thus DHT migrates into hair cells in the lower follicle and induces apoptosis to inhibit hair growth and shorten the anagen period.

Consistent with this finding is the one by Orentriech [76] that pilosebaceous units that grow thick terminal hairs when surgically transplanted to a region that is hairless will continue to grow thick terminal hairs. In some cases thick terminal hairs will begin to grow, sometimes in isolation, in regions that are normally hairless, such as the growth of facial hair in women, etc. In other words, the

response to the androgens are dependent on the specific pilosebaceous unit which is often, but not always regionally dependent. These findings suggest that specific pilosebaceous units are somehow programmed to respond to androgens in a way that either induce baldness or grow hair possibly by means of different receptor proteins or another mechanism.

Different receptor proteins for stimulating or retarding hair growth help to explain several apparently disparate facts. In the case of males, at puberty, thick terminal hairs begin to grow in the axilla, the mons pubis and the beard areas. This action occurs in spite of increased levels of testosterone and contrasts to what occurs later (at about age 20 in males) when increased levels of testosterone in the scalp help to cause male pattern baldness. Hamilton et al. [77] also demonstrated that eunuchs when injected intramuscularly with testosterone propionate exhibit an increased growth of coarse sternal hairs and yet, eunuchs when castrated before age 20 show even less growth of beard hair than eunuchs castrated after age 21 [78], see Table 1.15.

The first experiment involving testosterone injection, suggests that this androgen can somehow induce or promote hair growth in the skin of the thorax tissues, as opposed to the scalp, where this same hormone inhibits hair growth. The second experiment among eunuchs shows that a decrease in testosterone level in some body regions, such as the beard area in males decreases hair growth. Additionally, it demonstrates that removal of two of the glands that produce this hormone prior to the maturation of the local tissue (e.g., the scalp) responsible for hair growth, then hair growth will be further inhibited in that tissue. In other words, hair growth is dependent on the local tissue (most likely through specific receptor sites in the tissue) as well as the androgen level.

Epidermal growth factor receptors have been detected in the outer root sheath and in the epidermal papilla by Wollina and Knopf [79] and epidermal growth factors have been linked to the anagen to catagen transformation as shown by Philpott and Kealey [80]. Receptors for thyroid hormone have also been detected in keratinocytes by Mackenzie [81].

In addition to hormonal control and molecular signaling compounds, vitamins and retinoids, and mesenchymal components have been shown to help control the development of follicles and to maintain hair growth. These are fruitful areas of hair growth research. For entries into this literature, see the references by Alonso and Fuchs [12], Reddy et al. [67], Mackenzie [81], Hebert [82], Stenn [83] and Blumberg and Tonnic-Canic [84] and the following references [11–21].

Retinoids including vitamin A, retinol and retinoic acid play an important role in the growth and development of epithelial tissue. In excess, vitamin A and its

Table 1.15 Beard hair growth; before and after castration [78]

Group examined	Wt. Beard hair (mg/24 h) Ave. for ages 30–80
Normal controls	31.6
Castrated after age 21	13.7
Castrated before age 20	7.7

derivatives have been shown to inhibit keratinization [84]. This effect is likely related to DHT production. The sebaceous glands produce sebum that contains DHT. At too high a level, DHT inhibits hair growth and when used with minoxidil it has been shown to increase the effectiveness of the latter. This effect may be related to proper control of sebum production and DHT levels.

Vitamin D3, however, promotes keratinization [84]. On the other hand, there are no scientific studies on healthy subjects demonstrating the effects of dietary vitamins on hair growth. In the case of dietary insufficiency, there are indications that folic acid (a B-complex vitamin) and pyridoxine (a B-complex vitamin, B6) "may" be helpful to hair growth. Reis [85] described a role in cystine metabolism for these vitamins. Panthenol the precursor to pantothenic acid (another B-complex vitamin) has not been demonstrated to affect the growth or development of hair either in a dietary study or through topical application. Other materials known to either inhibit or promote hair growth are listed in Table 1.14. Eflornithine a chemotherapy drug known to retard hair growth has been explored in a joint venture with Gillette and Bristol-Myers Squibb as the active ingredient for a topically applied prescription product to help control facial hair in women.

To summarize hair growth, human scalp hair grows at an average rate of approximately 15 cm (about 6 in. per year). The life cycle of a hair fiber consists of three stages—anagen (growth stage), catagen (transition stage), and telogen (resting stage when the hair is shed). The life cycle of a hair fiber is initiated by chemical messengers that act on stem cells in the bulge. Wnt proteins, Sonic hedgehog and other regulators play a primary role in the anagen phase. Hair growth is partially controlled by androgens and the local tissue most likely through specific receptor sites. Testosterone and DHT are the primary androgens that determine whether hairs increase or decrease in size with age and some other aspects of hair growth and hair loss. During various stages of growth, signaling molecules and metabolites are transported between the different cell layers of Fig. 1.6 to the site where they activate the tissues. In spite of the fact that each follicular unit can function independently, the response by the local tissue tends to be a regional response and it determines whether hairs grow or whether the hair cycle is shortened and ultimately leads to baldness.

Differences in anagen can vary from a few months to up to 8 years or longer. For normal terminal scalp hairs, 2–6 years anagen is an average growth time, producing hairs approximately 1 m long (~3 ft) before shedding. Human hair generally grows in a mosaic pattern, thus, in any given area of the scalp, one finds hairs in various stages of their life cycle. In a normal healthy scalp, the vast majority of hairs are in anagen (about 80–90%); although there are seasonal changes in hair growth, with maximum shedding (telogen) as Autumn approaches (in the Northern Hemisphere, August/September). In all forms of hair loss, there is a more rapid turnover to telogen, thus a larger percentage of hairs are in telogen. In addition, vellus hairs, characterize baldness, although a small reduction in the number of follicles per unit area also occurs. For additional details regarding the biological syntheses and formation of human hair, see references [9–21, 26, 68–70, 75, 79–89]. Different treatments for hair loss are described in the next sections of this chapter.

1.6 Treatments for Hair Loss

Studies are currently underway to identify the genes involved in androgenetic alopecia, alopecia areata and alopecia totalis and alopecia universalis. As of late 2003, only one gene involved in androgenetic alopecia had been identified, that is the androgen receptor (AR) [90]. However, a lot of good work has been accomplished since that time. A summary of the science related to the role of genes and their products in relation to different types of baldness is described in Chap. 3 in the section entitled, *Some Other Hair Traits Related to Genetics*. If you are interested in this area, see references [90–93], the references in that section of Chap. 3 and read current works by the following scientists: Barahmani, N., Botchkarev, V., Brent-Richards, J., Christiano, A., Cotsarelis, G., Cox, G., Dawber, R.P.R., Duvic, M., Ellis, J.A., Fuchs, E., Harrap, S., Hillmer, A.M., Lui, H., Rogers, G., Rothnagel, J.A., Sawaya, M., Shapiro, J., Sinclair, R., Sundberg, J., Tang, L. and Whiting, D.A.

1.6.1 Surgical Treatment of Hair Loss

Several surgical procedures have been used for treatment of hair loss. Although these procedures may be used for most forms of alopecia, they are used primarily for treatment of androgenetic alopecia or for hair loss due to tissue injury such as burns, particularly in cases where extensive baldness exists. These procedures are based on the fact that hairs actively growing in one region of the scalp, such as the occipital region when moved with local tissue to a bald region will continue to grow as they did in the occipital region. These procedures confirm the role of local tissue control in the hair growth process. Current surgical treatments include:

- Hair transplantation
- Scalp reduction
- Transposition flap
- Soft tissue expansion

In the most common form of hair transplantation, small skin plugs containing 15–20 growing terminal hairs each are surgically removed and placed into a smaller cylindrical hole in the balding region of the scalp. Usually several sessions of transplantation are required involving the placement of 50 or more plugs per session. The placement or angling of the plugs is important to the end cosmetic effect. Elliptical grafts or even smaller mini-grafts may be employed and have been described by Shiell and Norwood [94]. Within 2–4 weeks after transplantation, the donor hairs usually fall out and are replaced by new hairs.

Lasers have been introduced into hair transplantation providing several advantages. Erbium and CO_2 lasers have been used. More advantages have been shown by the erbium laser. It allows for a smaller graft and offers the potential to create closer sites for more aesthetic results. Both techniques provide virtually

bloodless surgery and reduce operating times compared with conventional techniques. A diode laser was cleared by the FDA in 1998 and is currently being used for hair removal. This laser functions with 800 nm light and has a cooling device for patient comfort. It provides safe and effective hair removal with virtually no scarring and a decrease in the delay for hair re-growth.

Oftentimes, in cases where the bald area is rather large, scalp reduction is done in conjunction with hair transplantation. This method involves surgical excision of a strip of the bald skin to reduce the total hairless area. Repeated scalp reductions can be performed together with transplantation to provide better coverage for a very bald person.

The transposition flap method [95] involves moving a flap of skin that contains a dense area of hair to a bald area. This method is sometimes employed together with mini-graft implantation along the frontal hairline to provide a more natural appearance.

Soft tissue expansion is another surgical development for treatment of alopecia. In this procedure, soft silicone bags are inserted under the skin in the hair-bearing area of the scalp, usually in the occipital region. The bags are then slowly filled with salt water during a 2–4 month time period. After expansion of the hair-bearing skin, the bags are removed and the bald area of the scalp is excised and flaps are created with the expanded hair-bearing skin.

1.6.2 Hair Multiplication or Hair Induction Treatments for Hair Loss

Some novel and highly technical treatments for hair loss are being explored with encouraging but modest success. Some have referred to these treatments as cloning; however, cloning involves the production of a genetically identical organism. Cloning is clearly not what is being done for the growth of hair fibers (not an organism) on scalps. One successful technique described by Reynolds and Jahoda [96] was first called Trans-gender induction of hair follicles. This method has also been referred to as hair follicle cell transplantation. In this procedure portions of specific cellular structures such as dermal sheath cells are micro-surgically removed from actively growing hairs and injected into the skin of another person. The implanted cells act to promote the formation of new intact hairs. In the case described by Reynolds and Jahoda [96], the donor cells were from a male and implanted into a female, thus the name “transgender” induction. It would appear that some variation on this procedure offers potential as a treatment for hair loss. But, this procedure is only a laboratory curiosity and several steps are necessary to determine if this type of treatment can be brought to fruition. Unger [97] described current concepts, techniques and the future of transplantation in a paper published in the Journal of Investigative Dermatology.

1.6.3 Hair Extensions or Hair Weaves

This technique of adding or attaching hair to your own hair to provide different styles or looks has become popular. Hair extensions originated and were first made popular among African American women such as Janet Jackson, however women of all races today are taking advantage of the styles and looks that weaves provide, if they can afford it. There are several basic techniques for applying hair extensions:

The fusion method sometimes called infusion: This method involves gluing individual hairs; strand by strand or micro-braids to the subject's own strands of hair. Hair strands can be purchased with pre-applied adhesive that must be heated or glue sticks that require heating with a device similar to a glue gun to activate the adhesive. Infusion is the most expensive hair extension method because it takes 8–16 h to manually complete. This process lasts several months allowing contact with water such as shampooing once a week and even swimming.

Bonding involves gluing large strips of hair sometimes called wefts to the roots of the subject's own hair. Bonding glue and remover are sold along with wefts for this process. Bonded hair should not be left in place longer than 1 or 2 weeks because of stress on the roots.

Weaving is a process where a corn row or a track is created around the head with the subject's own hair. Extension hair is then sewn or woven onto the tracks and the subject's own hair lays over the tracks for a natural look.

Netting is where natural hair tresses are braided or woven onto a thin breathable net that fits onto the scalp. Netting can last up to 3 months, however care must be taken to dry the subjects own hair to avoid mildewing.

Because hair extensions provide for a natural look and optional styles they have become popular among female entertainers such as Beyonce, Janet Jackson, Britney Spears, Paris Hilton, Jessica Simpson and many others.

1.7 The Cuticle, Cortex, Medulla and Cell Membrane Complex

1.7.1 The Cuticle

The cuticle is a chemically resistant region surrounding the cortex in animal hair fibers (see Figs. 1.3, 1.7 and 1.8). Geiger [98] described its chemical resistance in the following manner. When isolated cuticle material and whole wool fiber are completely reduced and alkylated, the alkali solubility [99] of the cuticle material is approximately one-half that of whole fiber (85%). Cuticle cells are generally isolated from keratin fibers by shaking in formic acid [100], by enzymatic digestion [98, 101, 102], or by shaking in water [103]. Atsuta et al. [104] successfully applied the method of Taki for removing cuticle cells from wool fiber to remove cuticle

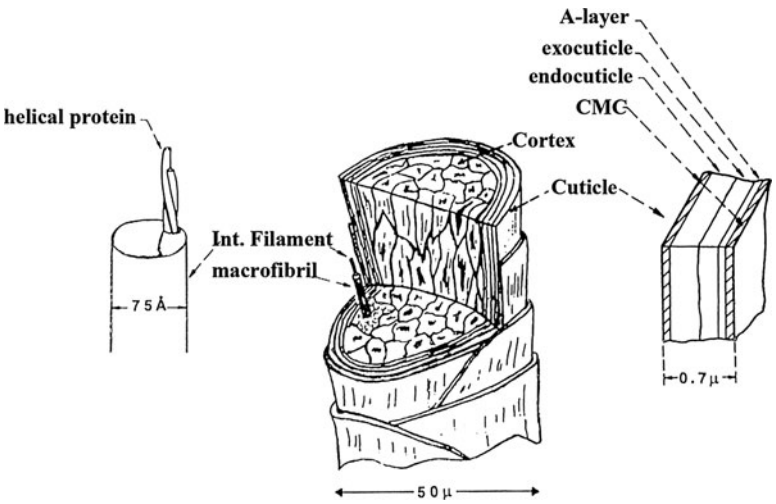

Fig. 1.20 Stereogram of the hair fiber structure, illustrating substructures of the cuticle and the cortex

from human hair fibers. This method involves shaking hair fibers for several hours with 5–6% potassium hydroxide in 1-butanol.

The cuticle consists of flat overlapping cells (scales) that surround the central fiber core (Figs. 1.8, 1.20, and 1.21). The cuticle cells are attached at the proximal end (root end), and they point toward the distal end (tip end) of the hair fiber, like shingles on a roof. The shape and orientation of the cuticle cells are responsible for the differential friction effect in hair (see Chap. 9). Each cuticle cell is approximately 0.5 μm thick, with about a 6–7 μm exposed axial surface or scale interval, and approximately 45–60 μm long. A comprehensive study by Takahashi et al. [105] on about 200 Asians and 200 Caucasians showed an average scale thickness of 0.45 μm for Asians and 0.43 μm for Caucasians, a surface cuticle interval of 6.61 μm for Asians and 6.98 μm for Caucasians within 1 cm of the scalp. The scale interval is in agreement with earlier data by Hardy [91] showing slightly more scales per 0.52 mm for Asians (15.47) vs. Caucasians (15.07) and more scales per unit length for people of East African descent (17.92). See the section in Chap. 9 entitled *Scale Type of Mammalian Hairs is Related to Hair Fiber Diameter*.

The cuticle in human scalp hair is generally 6–8 scales thick for Asians and Caucasians with slightly more scales in Asians as shown in a study by Hardy [106] and Takahashi [105]. Other studies with fewer subjects show variation from about 5 to 10 cuticle layers [100, 101]. The schematic of Fig. 1.22 by Alan Swift [107] illustrates similar dimensions and the layering of the cuticle. Woods and Orwin [108] describe the formation of the single layer of overlapping scales in most wool fibers that is sometimes described as 1–2 scales thick. The number of scale layers can serve as a clue to the species of origin in forensic studies.

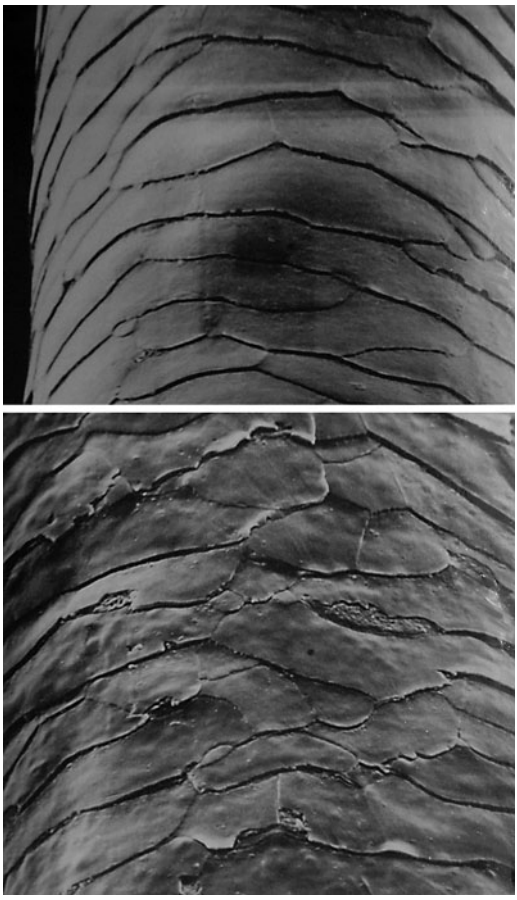

Fig. 1.21 Cuticle scales of human hair. *Top*: Near root end and close to the scalp. Note smooth scale edges. *Bottom*: Near tip end of another fiber. Note worn and broken scale edges

The cuticle of virgin human hair contains smooth unbroken scale edges at the root or proximal end near the scalp (see Fig. 1.21). Cuticle damage evidenced by broken scale edges can usually be observed a few centimeters away from the scalp. Such damage is caused by weathering and mechanical damage from the effects of normal grooming actions, such as combing, brushing and shampooing (Figs. 1.21 and 1.23). In many long hair fibers (25 cm or longer), progressive surface damage may be observed (illustrated by Fig. 1.23). Stage 1 shows intact smooth scale edges and scale surfaces; stage 2 contains broken scale edges; in stage 3, the scales have been partially removed, and in stage 4 the hair splits indicating extensive cortical damage. Garcia et al. described this phenomenon of hair degradation in some detail [109]. See Chap. 6 for additional information and references on this important phenomenon.

The cuticle of both human hair and wool fiber has been shown to contain a higher percentage of cystine than whole fiber [110] and more of the other amino acids that are generally not found in alpha-helical polypeptides [111]. Analysis of the cuticle

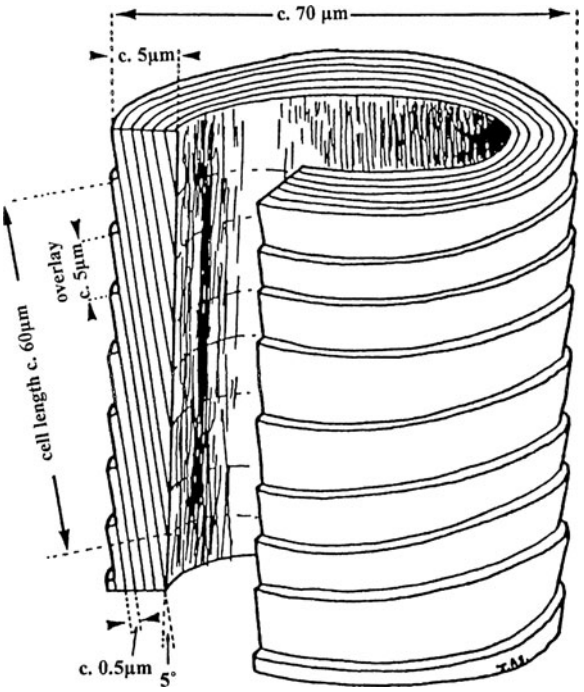

Fig. 1.22 A schematic diagram of the human hair cuticle illustrating its dimensions and layering, by J. A. Swift [107] (Reprinted with permission of the Journal of Cosmetic Science)

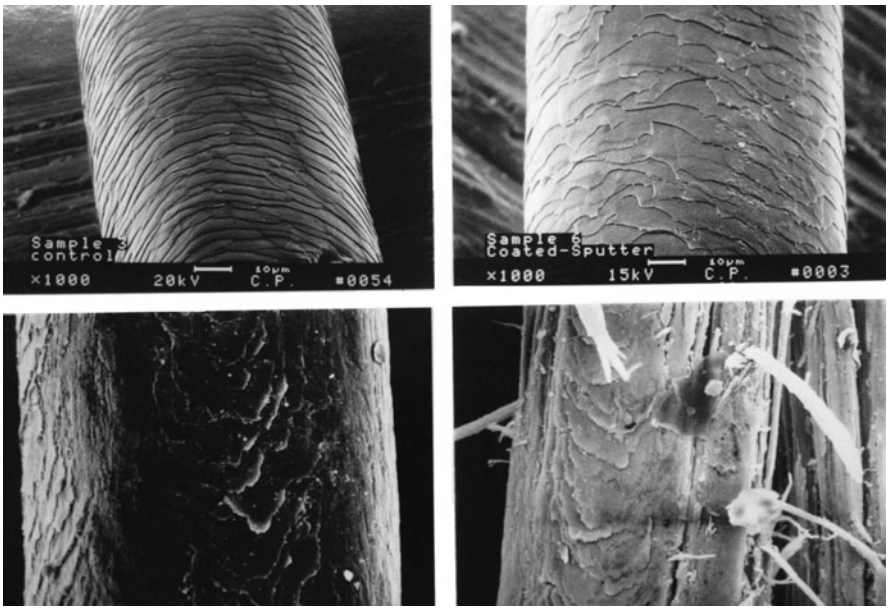

Fig. 1.23 Weathering and cuticle wear. *Top left*: Stage 1, note smooth cuticle edges. *Top right*: Stage 2, note broken cuticle scale edges. *Bottom left*: Stage 3, note complete removal of cuticle (*central area*). *Bottom right*: Stage 4, split hair

of wool fiber by the polarizing microscope shows negligible birefringence [1]. The cuticle of human hair also demonstrates negligible birefringence. Astbury and Street [112] provided x-ray evidence confirming that, in contrast to the cortex; the cuticle of hairs does not contain crystalline domains and as such is not as highly organized at the molecular level as the cortex.

1.7.1.1 The Different Layers of the Cuticle

The schematic diagram of Fig. 1.24 illustrates the internal structure of cuticle cells. The uppermost structure of each cuticle cell contains a thin proteinaceous membrane, the epicuticle that is covered with a lipid layer that includes 18-methyl eicosanoic acid. Different estimates of the thickness of this lipo-protein membrane have been cited [113, 114]; however, 10–14 nm by Swift and Smith [115] is probably the best current estimate. See the section entitled the *Cell Membrane Complex including the Intercellular Matter and the Nonkeratin Regions of Hair* in this chapter and Chap. 2 on this same subject. See also the schematics in that same section in this chapter and the section in Chap. 6 entitled *The Hair Fiber Surface*.

Beneath the cuticle cell membranes are three major layers; the A layer, a highly cross linked resistant layer about 50–100 nm thick (see Fig. 1.24). The A layer contains a high cystine content (>30%) and additional cross links called isopeptide bonds found by Zahn et al. [116]. Isopeptide bonds are created by reaction of glutamine with lysine under the influence of a transglutaminase enzyme. The exocuticle, sometimes called the B layer, is beneath the A-layer. It is also rich in cystine (~15–20%) and highly variable in thickness in each cuticle cell averaging about 150 nm. Underneath the exocuticle is the endocuticle, low in cystine content (~3%) [107] and also highly variable in thickness from about 50 to 300 nm within each cuticle scale [107] (see Fig. 1.24). Figure 1.25 is a transmission electron

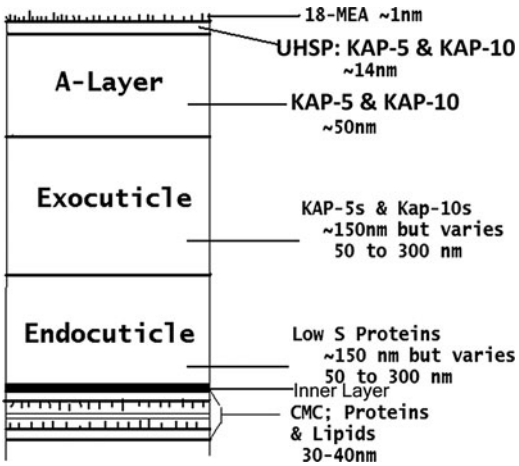

Fig. 1.24 Schematic diagram of the proposed structure of a cuticle cell in cross section

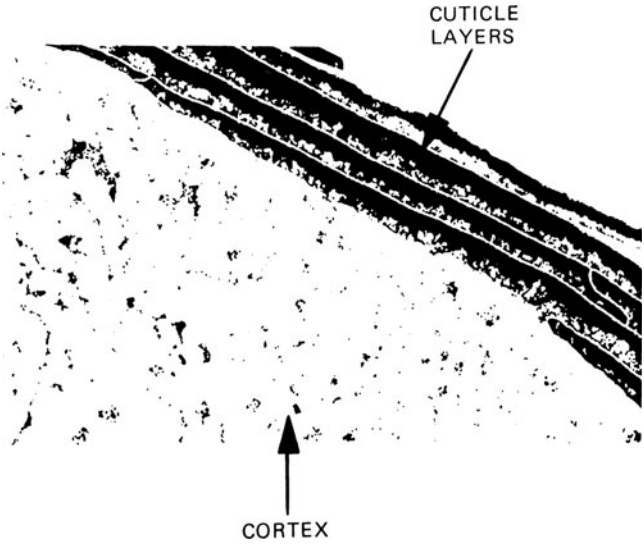

Fig. 1.25 TEM of a cross section of a hair fiber treated with silver methenamine, illustrating high and low sulfur layers of cuticle cells (stained = high-sulfur regions) (Kindly provided by R. Wickett and B. Barman)

micrograph illustrating the high sulfur (cystine) and the low sulfur regions of these layers through a staining reaction with silver methenamine. This stain marker stains the high sulfur regions of the cuticle cells, that is the epicuticle, the A-layer and the exocuticle. For additional details on the chemical composition of these three important layers of the cuticle, see Swift and Bews [117] and Chap. 2.

A portion of the under-membrane of Fig. 1.24 is also epicuticle or "epicuticle-like" matter. The cystine rich proteins of the cuticle are either high sulfur or ultra high sulfur proteins. Structurally different, high sulfur and ultra high sulfur proteins are found in the cortex. See the section entitled *Major Protein Fractions of Hair* in Chap. 2.

The cuticle of human hair is a laminar structure similar to the cuticle of wool fiber. Details of the different layers of the cuticle have been described for merino wool and for human hair in these references [109, 118–121]. Figure 1.24 illustrates the laminar structure of each cuticle cell. Figure 1.26 illustrates the "initial" view of the laminar structure of the cell membrane complex of the cuticle (cuticle-cuticle cell membrane complex) and Fig. 1.27 illustrates the cuticle structure relative to the whole fiber. The cell membrane complex and endocuticle represent vulnerable regions to the chemical and physical interactions of permanent waves, bleaches (including permanent dyes) and to everyday grooming actions. See Chap. 6 for a more complete discussion of this subject. Chap. 2 contains a more complete description of the amino acid and protein compositions of the cuticle and its different component parts.

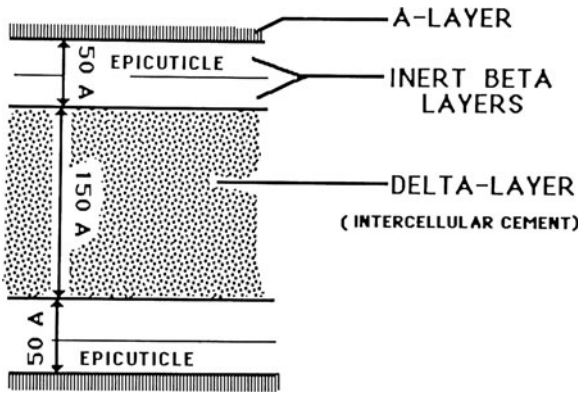

Fig. 1.26 Schematic illustrating cell membrane complex in animal hairs (Adapted from Fraser et al. [124])

1.7.1.2 Epicuticle and the Hair Fiber Surface

Negri et al. [122] demonstrated that the outer surface of hair fibers consists of about 75% of a heavily cross-linked protein and about 25% fatty acid that is predominantly 18-methyl eicosanoic acid. These authors proposed a model wherein the fatty acid layer (lipid layer) is connected to the underlying fibrous protein layer through thioester linkages involving the cysteine residues of the underlying epicuticle proteins [122, 123], see Fig. 1.28.

Negri et al. [123] also demonstrated that alcoholic alkali and chlorine treatments remove the fatty acid layer from the cuticle. These scientists concluded that the attachment of 18-methyl eicosanoic acid is through thioester linkages because chlorine water should not remove this lipid layer if it were attached through an ester or amide linkage; however chlorine water will readily cleave thioester bonds. Related layers exist between cortical cells that are unstained with protein stains, but these are removed by soxhlet extraction with chloroform-methanol. Extraction with this lipid solvent suggests that covalent attachment is not involved in the complex lipid layers between cortical cells [123]. See the section in this chapter entitled, the *Cell Membrane Complex including the Intercellular Nonkeratin Regions of Hair* and Chap. 2 on this same subject for a more complete description of the cell membrane complex.

So, the surface of mammalian hairs is covered with a thin covalently bound lipid layer of 18-methyl eicosanoic acid that is bonded to a proteinaceous cell membrane called epicuticle [124]. Jones and Rivett [125] concluded that Sims and XPS "indicate the surface of wool fibers is almost exclusively hydrocarbon" consisting of 18-methyl eicosanoic acid and free lipids (see Chap. 2 for details). This protein membrane is approximately 13 nm thick [114] (see Figs. 1.24, 1.25, 1.26, 1.27). In Fig. 1.24, the surface cell membrane consists of the epicuticle (proteins) and the 18-methyl eicosanoic acid which is sometimes called the upper or outer Beta layer. Since the attachment of 18-methyl eicosanoic acid to hair is through thioester linkages and the cell membrane protein is cross linked by cystine linkages, the methyl eicosanoic acid must be attached to an ultrahigh sulfur protein.

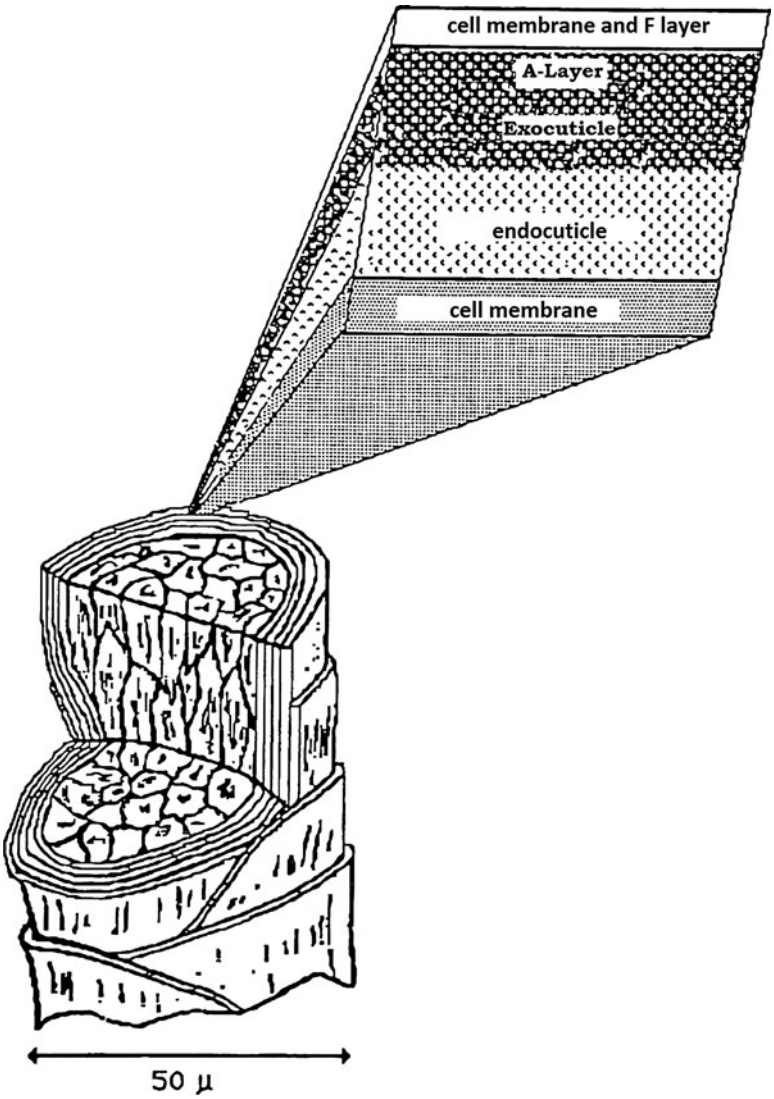

Fig. 1.27 Schematic diagram illustrating cuticle layers with respect to the whole fiber

As hair is exposed to repeated washing, drying and rubbing actions and to sunlight, changes occur in these surface layers leading to the formation of sulfur compounds and acids such as mercaptan, sulfinate and sulfonate groups. These actions lead to a decrease in the free and bound lipid content of the surface thereby converting the virgin hair surface from a hydrophobic, entity with little surface charge to a more hydrophilic, more polar and more negatively charged surface, see Chap. 2 and the discussion in Chap. 6 for more details.

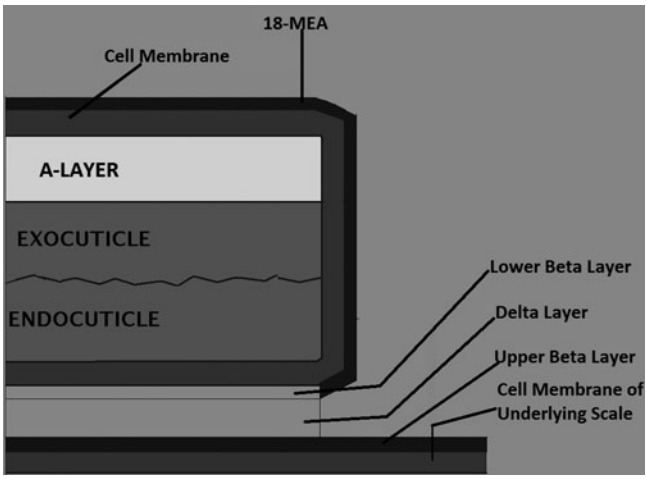

Fig. 1.28 Schematic illustrating lipid structures in the surface and CMC of the cuticle of hair

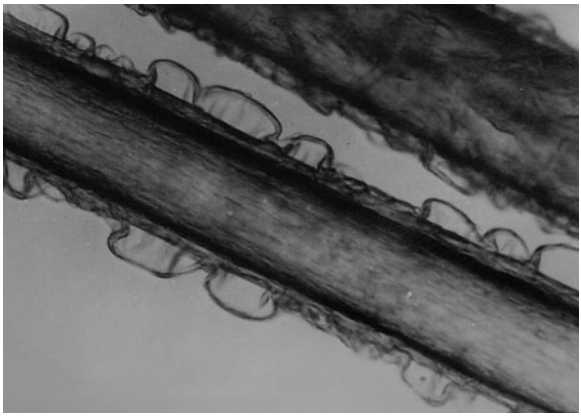

Fig. 1.29 Allworden sacs formed at the surface of hair fibers during reaction with chlorine water

More than 90 years ago, Allworden [126] observed that sacs or bubbles form at the surface of the fibers during treatment with chlorine water (see Fig. 1.29). Chlorine water diffuses into cuticle cells and attacks thioester linkages removing the lipid layer from the hair surface. It further degrades the proteins beneath the epicuticle by attacking the disulfide bonds cleaving the protein cross links and oxidizing them to higher sulfur acids producing water-soluble species too bulky to diffuse out of the semipermeable membrane. Swelling then results, due to osmotic forces, producing the characteristic Allworden sacs [122, 127].

After removal of the surface lipids, wool fiber still undergoes the Allworden reaction [122]. This fact confirms that these surface lipids are attached to the cell membranes of the cuticle, and furthermore their removal alters but does not destroy

the cuticle cell membranes. At this stage the primary integrity of the membrane is most likely due to the resistant isopeptide cross-links in the cuticle cell membranes.

Leeder et al. [128] provided evidence that the cell membrane lipids of wool fiber do not consist of phospholipids that normally form bilayers in living tissue. It was suggested at one time that the epicuticle is a continuous membrane covering only the very fiber surface [129]. However, Leeder and Bradbury [100] isolated single cuticle cells from wool fiber and demonstrated that single cuticle cells undergo the Allworden reaction, thus proving that this membrane surrounds each cuticle scale. What has been described as a continuous epicuticle may be cell membrane complex, consisting of epicuticle and intercellular binding material that could produce the appearance of a continuous sheath.

Of the methods described for isolation of epicuticle, first and foremost is the method by Lindberg et al. [129]. This method involves treatment of intact fibers with chlorine water or bromine water followed by neutralization and shaking and is a modification of the Allworden reaction. Another method, by Langermalm and Philip [113] involves dissolving the bulk of the fiber from the membrane with dilute sodium sulfide. Neither of these procedures produces pure epicuticle, but they probably provide cell membrane material and part of the underlying A-layer.

Swift and Holmes [114] described a relatively nondestructive method involving extraction with hot ethanol for removing some epicuticle material from human hair fibers. These same scientists concluded that the epicuticle of hair contains both lipid and fibrous protein layers, and is cell membrane material but does not have sufficient contrast with its surroundings to allow microscopic identification. Hair fibers, when extracted extensively with hot ethanol, are less resistant to enzymatic degradation than ether-extracted hair and do not undergo the characteristic Allworden reaction with chlorine water. It has been suggested therefore that extraction of hair with hot ethanol removes either a portion of or degrades the epicuticle membrane sufficiently to prevent the Allworden reaction from occurring. Chemical analysis of epicuticle-like substance removed from hair by hot ethanol extraction shows that both protein and fatty acids are present (20–30%) [130, 131]; qualitatively similar results have been reported by Leeder and Bradbury for analysis of epicuticle isolated from merino wool [100].

Allworden membranes have been isolated and analyzed quantitatively for amino acid content by Allen et al. [132] who found approximately 21% half-cystine in these isolated membranes. Additional details of the amino acids and their quantities found by Allen et al. and by others are described in Chap. 2.

Zahn et al. [133] used Allen's amino acid data for Allworden membranes and known compositions of loricrin, involucrin and an ultra high sulfur protein in a multiple regression analysis. This statistical procedure provided indirect evidence for 51% ultra high sulfur protein, 42% loricrin and 7% involucrin in Allworden membranes. Zahn et al. suggested the possibility of a relationship between the membranes of hair and the cellular envelope of skin which also contains loricrin and involucrin. But, more recent evidence by Rogers and Koike [134] rules out loricrin and involucrin in the epicuticle suggesting strongly that 18-methyl

eicosanoic acid is attached to an ultrahigh sulfur protein most likely of the KAP 5 or 10 types which are cross-linked via cystine and also by isopeptide bonds.

Leeder et al. [135] defined the epicuticle as a chemically resistant proteinaceous membrane that remains on keratin fiber surfaces after strongly bound lipids have been removed with potassium t-butoxide in anhydrous butanol. Thus, the epicuticle is a proteinaceous layer about 130 Å thick covered by a strongly bound structural lipid that Leeder called the F layer (18-methyl eicosanoic acid). The F layer is not a frequently used term today, but it represents the outermost lipid layer of the fiber surface.

Several different laboratories have analyzed the outer surface of wool and human hair via XPS examining the outer 2–3 nm of the hair surface [136–139]. Ward et al. [136] estimated the thickness of the lipid layer of 18-methyl eicosanoic acid at 1 ± 0.5 nm. From Carbon/Nitrogen analysis, assuming XPS examines the top 3 nm, Carr et al. [139] estimated 60% protein and 40% lipid in the top 3 nm of soxhlet extracted wool. This estimate provides for 36% 18-methyl eicosanoic acid (at 1.1 nm thick) and 4% Free Lipid in the top 3 nm of this wool sample. A similar estimate using data of Robbins and Bahl [137] provided 12% free lipid remaining after shampooing human hair. These data suggest that free lipid is an integral part of the surface of hair (most likely between 18-methyl eicosanoic acid molecules) after and between normal shampooing and hair treatments. See Chap. 2 for additional details.

Capablanca and Watt [140] examined wool fiber that had been washed with detergent and extracted with various solvents using a streaming potential method. These scientists found an appreciable effect of free lipid on the isoelectric point with surfactant washed wool having an isoelectric of 3.3 while the most effective lipid solvent extracted wool provided an isoelectric of 4.5. These data show that the true isoelectric point of the surface hair proteins is close to 4.5. Furthermore, free lipid which contains fatty acids is an important and essential component of the surface of animal hairs, especially for hair in good condition that has only been cleaned with shampoos. Furthermore, the more free lipid (fatty acid) in the surface layers, the lower the isoelectric point of the fibers.

We know that the surface of hair contains 18-methyl eicosanoic acid attached to a fibrous ultra high sulfur protein and the source of this surface is the cuticle-cuticle cell membrane complex. Furthermore, we know that the thickness of the upper Beta layer in the cuticle-cuticle cell membrane complex is about 3 nm [141–143]. However, the thickness of the lipid layer on the surface of wool fiber measured on exhaustively extracted hair by Ward et al. [136] using XPS was about 1 nm. Zahn et al. [116] proposed a model to explain this smaller than expected thickness of the MEA in which the surface chains of MEA fold back on themselves. Recently, Natarajan and Robbins [144] through computer modeling calculated an MEA layer on a KAP-5 ultra high sulfur protein backbone to be 1.08 nm thick in excellent agreement with the calculations by Ward et al. [136].

XPS shows that shampooed hair and scoured wool contain more lipid at the surface than can be accounted for by MEA alone. Furthermore, wool extracted by different solvents provides different isolectric points suggesting that free fatty

acids/lipids are in the top 3 nm of the hair surface. Therefore it is reasonable to conclude that in the cell membrane complex of the cuticle and in the virgin most surface there is free fatty acid in between MEA molecules causing it to stretch out to approach its full length of about 2.75 nm at an angle of 72° and with additional assumptions provides a lipid layer thickness close to 3 nm, see the section in this chapter entitled *Thickness of the Cuticle Beta Layers*. This value is in agreement with the thickness of the upper Beta layer [141, 142] that ultimately becomes the major part of the new hair fiber surface when hair is deformed and abraded in the dry state [107].

1.7.2 The Cortex, its Cells, Macrofibrils, Matrix and Intermediate Filaments

The cortex constitutes the major part of the fiber mass (70–90%, the lower percentage in fine hair) of human hair and consists of cells and intercellular binding material. The intercellular binding material or the cell membrane complex is described later in this chapter.

1.7.2.1 Cortical Cells

Randebrock [2] found that cortical cells of human hair fibers are generally 1–6 μm thick and approximately 50–100 μm long (see Figs. 1.20 and 1.30), although considerable variation in their size and shape has been reported. Figure 1.30 is an SEM of a split hair with separated cortical cells appearing like splintered wood. Figure 1.31 is a high magnification image of the same split hair illustrating the macrofibrillar structures inside cortical cells. Straight to wavy Caucasian hair contains a more symmetrical cortex, like straight mohair fiber, and most (but not all) of the cells are of the same general type with regard to the ratio of fibrillar to nonfibrillar matter (highly crystalline = fibrillar; less organized = nonfibrillar).

Many wool fibers contain two or even three types of cortical cells that are sometimes segregated into distinct regions (Fig. 1.32) that can be observed in cross section [145]. These cell types are called orthocortex, paracortex, and mesocortex. Orthocortical cells contain less matrix material between the intermediate filaments and lower sulfur content (~3%). Kassenbeck [146] indicated that paracortical cells are smaller in diameter, and they have smooth and rounded borders and higher sulfur content (~5%) [146]. Mesocortical cells contain intermediate cystine content [147].

Morphologically, the cortical cells of human scalp hair of Caucasians are similar but not identical to those of wool fiber. Kassenbeck [146] determined that cortical cells adjacent to the cuticle in human hair are more flat and contain less sulfur than the remaining cortical cells that comprise the bulk of the cortex. Kassenbeck calls

Fig. 1.30 SEM of a split hair. Note cortical cell fragments

these heterotype cortical cells. Leon [148] several years ago noted in his review on hair that "Negro" hair contains a higher proportion of orthocortex cells than Caucasian hair. Swift [149] more recently provided evidence on a limited sampling of Nigerian hair for a higher percentage of orthocortical type cells (roughly 50/50 para to orthocortex) than in straight hair of Caucasians which he classified as predominately paracortex with a small arc (about 1 cell thick) of orthocortex at the periphery somewhat similar to Kassenbeck's description of Caucasian hair.

Thibaut et al. [150] and Bryson et al. [151] investigated the different types of cortical cells and their structures in more detail and identified different distributions of different cell types for straight vs. curly hair. Their findings are summarized in this chapter in the section entitled *The Origin of Hair Fiber Curvature*.

Kassenbeck [146] suggested that the biological function of crimped animal hairs is to trap large volumes of air in the hair coat to provide thermal insulation. For animals with both summer and winter fur: Summer fur—begins to grow rapidly in the spring, producing long and coarse hairs that are less crimped to inhibit the formation of air pockets and to permit cooling.

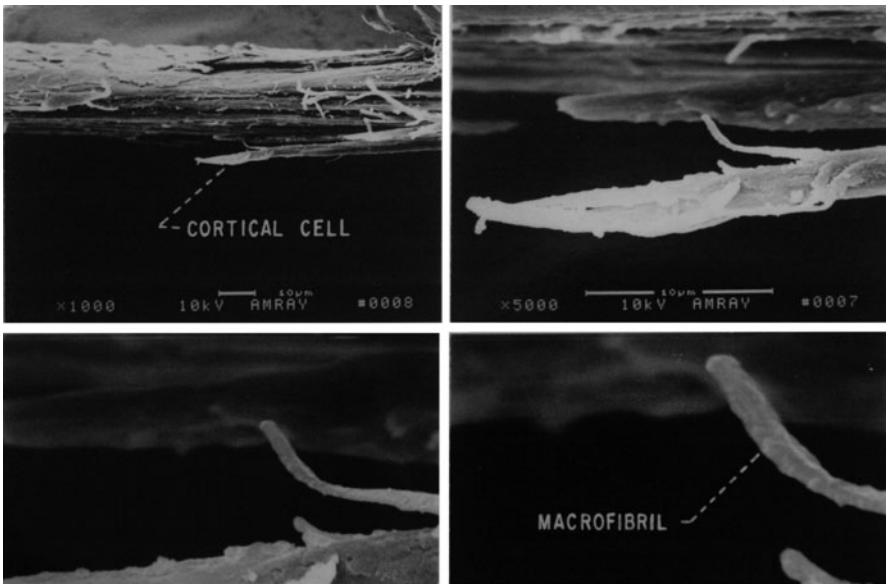

Fig. 1.31 Scanning electron micrograph of a split hair showing details of cortical structure

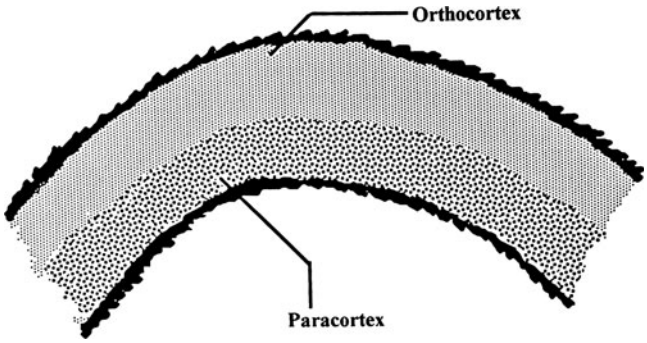

Fig. 1.32 Schematic of a wool fiber, illustrating orthocortex and paracortex regions of the cortex in relation to crimp

Winter fur—begins to grow in the autumn, yielding short, stiff, crimped hairs to trap large volumes of air in the coat for thermal insulation. Perhaps the seasonal effect on anagen/telogen ratios for human scalp hair is related to the summer/winter effects on hair growth in fur bearing animals.

Kassenbeck [146] further explained that the growth rate of animal hair and the morphological structures of both cuticle and cortex are relevant to the hair shape and to the cooling and insulation functions. Cortical cells also contain pigment granules and nuclear remnants. The nuclear remnants are small, elongated cavities near the center of the cells. The pigment granules are small, oval or spherical

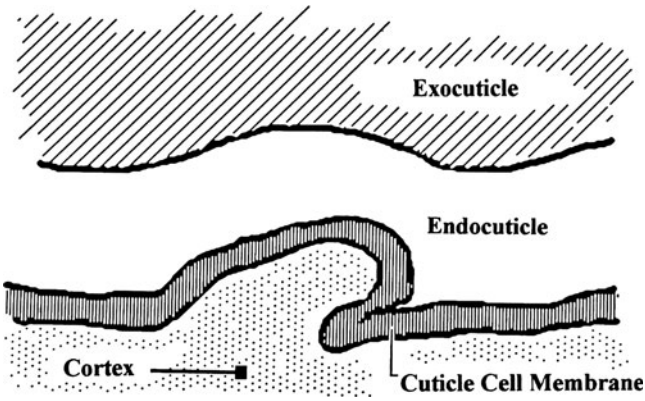

Fig. 1.33 Schematic illustrating Piper's interlocking scheme for linking cuticle to cortex

particles of approximately 2,000–8,000 Å units (0.2–0.8 μm) in "diameter" [152] that are dispersed throughout the cortical and medullary cells. Both these structures comprise only a small fraction of the cortex. Generally, pigment granules do not occur in the cuticle of scalp hair; however, pigment granules have been observed in the cuticle and the medulla of beard hair, especially in heavily pigmented hair [5].

Birbeck and Mercer [153] suggested that pigment granules enter the cortical cells by a phagocytosis mechanism in the zone of differentiation and biological synthesis. Piper [154] presented evidence that cortical cells are linked to adjacent cuticle cells via complex interlocking structures occurring through a mechanism involving phagocytosis (see Fig. 1.33).

Cortical cells may be isolated from human hair by procedures involving either shaking in formic acid [100, 155], or other solvents (Erhardt H, Private communication), or enzymatic digestion [98, 101, 102]. Another procedure involves shaking hair fibers in water in the presence of glass beads by Wortmann [103] to strip the cuticle cells from the hair to provide cortex with intact cell membranes free of cuticle. In addition to nuclear remnants and pigment granules, the cortical cells of human hair contain highly important spindle-shaped fibrous structures called macrofibrils or macrofilaments (see Figs. 1.20, 1.31 and 1.34).

1.7.2.2 Macrofibrils

Randebrock [2] followed up on the pioneering studies of George Rogers on wool and other hair fibers and found that the spindle-shaped macrofibrils in human hair are approximately 0.1–0.4 μm in width or diameter. The macrofibrils comprise a major portion of the cortical cells (see Figs. 1.34 and 1.35). Each macrofibril consists of intermediate filaments originally called microfibrils (highly organized fibrillar units) in a matrix, a less organized structure that surrounds the intermediate

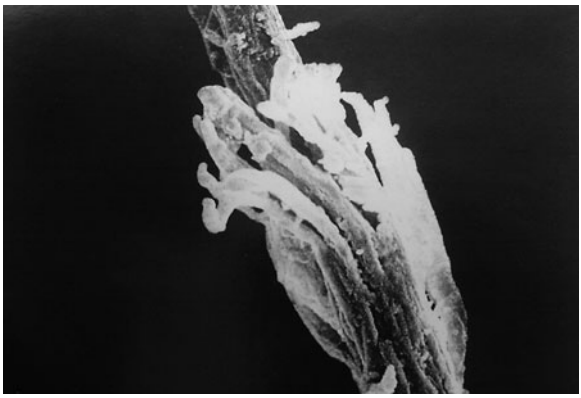

Fig. 1.34 Scanning electron micrograph of cortical cells of a human hair fiber. From a split hair

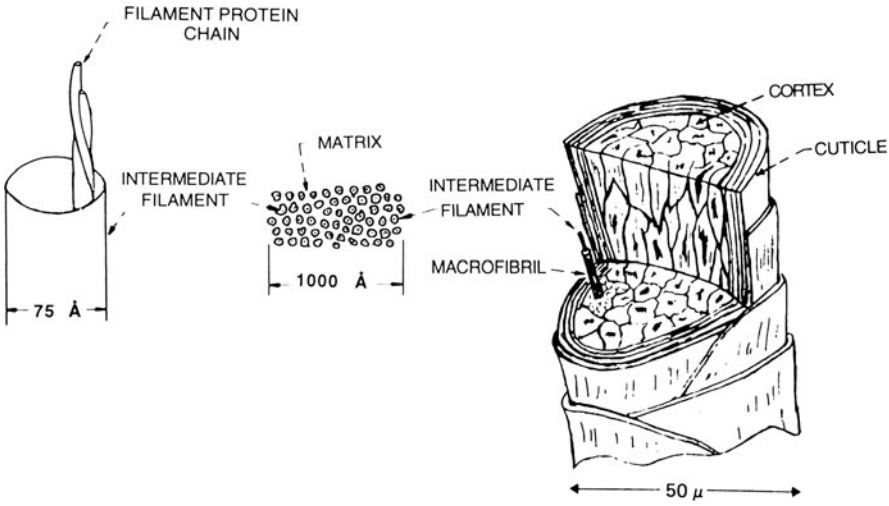

Fig. 1.35 Stereogram of a human hair fiber including intermediate filament-matrix structures

filaments. For more details on the intermediate filament structures see the section entitled *Intermediate Filaments* in this chapter.

1.7.2.3 Matrix

Various estimates of the relative quantities of matrix to intermediate filament protein (amorphous to crystalline proteins) have been made for both wool fiber and human hair [156, 157]. Although the relative quantities vary [158], the matrix-to-intermediate filament ratio in human hair is generally greater than 1.0. Protein derived primarily from matrix (gamma keratose) can be isolated from keratin fibers by the method of Alexander and Earland [159]. See Chap. 2 in the section entitled

Other Protein Fractionation Methods. This method involves oxidation of hair using peracetic acid followed by alkaline treatment. Analysis of the gamma keratose from human hair indicates a higher proportion of sulfur compared to the other keratose fractions or to whole fiber [87]. Corfield et al. [160] isolated matrix material from merino wool by this procedure. Chemical analysis gave a relatively high proportion of sulfur and a correspondingly greater proportion of cystine compared to the other fractions or to whole fiber [87].

Electron microscopy takes advantage of the high cystine content of matrix and the ability of cystine to react with osmium tetroxide to reveal the fine structure of hair in the following manner. Reduction of the fibers followed by treatment with osmium tetroxide, prior to sectioning, produces a heavily stained matrix revealing the relatively unstained intermediate filaments [161].

Matrix comprises the largest structural subunit of the cortex of human hair fibers. It contains the highest concentration of disulfide bonds of the cortex and the majority of these are probably intra-chain bonds rather than inter-chain bonds, because the matrix swells considerably when wet with water. Mechanically the matrix resembles a lightly cross-linked gel [162] rather than a highly cross-linked polymer. Matrix is often referred to as the amorphous region; although evidence suggests that it does contain some degree of structural organization [163]. A spacing of 28 Å has been demonstrated in mohair matrix. Spei attributed this spacing to structural repeat units of the matrix [164].

Proteins of the matrix are sometimes referred to in the literature as keratin associated proteins (KAP's) or as inter-fibrillar associated proteins (IFAP). Rogers et al. [165] suggested that there are essentially three classes of KAP's based on amino acid composition. The high sulfur KAP's (containing about 20% to about 30% cystine), the Ultra high sulfur KAP's (containing approximately 30% or more cystine and about 20% or more serine) and the KAP 6–8 which are tyrosine/glycine rich KAP's, see the section entitled *The KAP Proteins of Human Hair* in Chap. 2 for more details about the KAP proteins in human hair.

1.7.2.4 Intermediate Filaments

As indicated above, the macrofibrils in human hair contain subfilamentous structures called intermediate filaments (IF) (formed from intermediate filament proteins or keratins) and originally called microfibrils (microfilaments). The macrofibrils are arranged in spiral formation in the cortical cells. The radius of each spiral of the macrofibril, is approximately 4,000-Å units [166], and the width or diameter of an intermediate filament is close to 75 Å (see Fig. 1.20).

Two of the six known Types of IF proteins are in keratin fibers. The exact organization within the IFs of hair fibers is still being determined, although several basic structures were proposed back in the 1980s [167, 168] and improved upon since then. The filamentous polypeptides of human hair fibers are classified as Type I and Type II and these differ by their amino acid sequences resulting in acidic (Type I) and neutral to basic (Type II) proteins. Crewther et al. [167] in 1983

concluded that the IFs contain precise arrays of the low-sulfur proteins, containing short sections of alpha-helical proteins in coiled coil formation, showing a heptad repeat unit. The coiled coils are interrupted at three positions by non-helical fragments and are terminated by non-helical domains at both the nitrogen (N) and carbon (C) termini of the chain (Fig. 1.36). The individual filament-like protein chains of Fig. 1.35 are arranged into coiled coil dimers each containing one strand of type I and a second strand of type II chains (Fig. 1.36). These coiled coil dimers are then coiled around other dimers forming tetramers and higher ordered tubular type structures with very complex molecular associations head to tail forming longer filaments and lateral associations across coils forming complex IF structures which ultimately produce the different protein domains of orthocortex, mesocortex and paracortex, etc.

The schematic of Fig. 1.36 shows a general structure for the initial formation of dimeric units of IF structures. In this schematic, at the end N terminus, E1 is the end domain, V1 is a variable sequence and H1 is a high sequence region. At the C terminus, E2 is the end domain, V2 is a variable sequence and H2 is a high sequence region. The cystine content, of the low sulfur region of an IF is about 6%. It is not uniformly dispersed between domains of an IF chain. The rod domain contains about only 3% half-cystine, which is about one half-cystine residue, while the N terminal domain contains about 11% half-cystine and the C terminal unit about

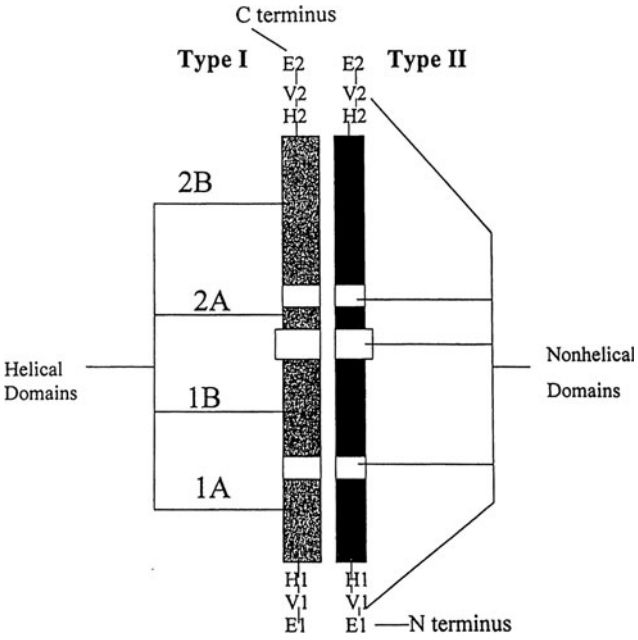

Fig. 1.36 Schematic illustrating the structure of an intermediate filament protein (type I-type II dimer). E are the end domains (E2 the C terminus and E1 the N terminus), V a variable sequence region and H is a high sequence region

17% half-cystine. Fraser [168, 169] suggested that these half-cystine residues are involved in disulfide linkages and that most of the disulfide residues exist in the matrix rather than in the IFs.

These dimeric units aggregate in an anti-parallel arrangement to form structural units composed of four protein chains or tetramers [167, 168]. Tetramers are connected end to end forming subfilaments called protofilaments which interact together to form the IFs of the cortex. Seven to ten of these tetramer units are believed to combine or aggregate into a larger helical structure, forming the IFs of the cortex of animal hairs. It would appear that the most favored structure is still the one proposed by R.D.B. Fraser et al. [168] in the 1980s. Fraser's concept contains a total of 8 protofilaments and consists of a single core protofilament surrounded by seven protofilaments [168]. For a more complete discussion of IF structures of keratin fibers, see the paper by ErRafik, Doucet and Briki on IFs of human hair [170], the paper by Powell and Rogers [89] and the references by Langbein and M. A. Rogers et al. in this chapter including [171, 172] and the papers by R.D. Bruce Fraser [173] and R.D.B. Fraser [174].

Langbein and M.A. Rogers et al. [171] reported that there are nine members in the human Type I subfamily that can be divided into three groups where H = hair, a = acidic, b = basic, and the number corresponds to a two dimensional staining spot. The names in parentheses are newer names as summarized in Table 1.16. Group A: hHa1 (K31), hHa3-I (K33a), hHa3-II (K33b), hHa4 (K34) and Group B: hHa7 (K37), hHa8 (K38) and Group C: hHa2 (K32), hHa5 (K35), hHa6 (K36). This latter group represents structurally unrelated hair keratins. Langbein and Rogers

Table 1.16 Nomenclature for the keratins found in the hair fiber and the hair follicle

Type I acidic		Type II basic to neutral	
Former name	Newer name	Former name	Newer name
Keratins found in the hair fiber itself			
hHa1	K31	hHb1	K81
hHa2	K32	hHb2	K82
hHa3-I	K33a	hHb3	K83
hHa3-II	K33b	hHb4	K84
hHa4	K34	hHb5	K85
hHa5	K35	hHb6	K86
hHa6	K36		
hHa7	K37		
hHa8	K38		
Ka35	K39		
Ka36	K40		
Hair follicle Keratins found in the root sheath			
K25irs1	K25	K6irs1	K71
K25irs2	K26	K6irs2	K72
K25irs3	K27	K6irs3	K73
K25irs4	K28	K6irs4	K74
		K6hf	K75

et al. [172] described that the Type II keratin subfamily contains six members divided into two groups and designated as: Group A: hHb1 (K81), hHb3 (K83), hHb6 (K86) which are structurally related and Group C: hHb2 (K82), hHb4 (K84) and hHb5 (K85) which are distinct. The sequence in which these keratins are expressed in the follicle is also described by Langbein and Rogers et al. in these papers. For additional details on these important hair proteins see Chap. 2 in the section entitled *Type I and II Keratin Proteins (IF Proteins) of Human Hair* and references [168–174].

1.7.2.5 Helical Proteins of the Intermediate Filaments

The subunits that constitute the IFs of hair fibers are polypeptide chains of proteins see Fig. 1.36 that are combined together as described in the section above. The coiled sections or the helical domains of these protein chains are approximately 10 Å in diameter, including side chains, and are believed to approximate the form of an alpha helix, first proposed by Pauling and Corey [175–177] (see Figs. 1.37 and 1.38).

Pauling and Corey proposed the alpha helix from the x-ray diffraction analysis of keratin fibers pioneered by Astbury et al. [178–180] and MacArthur [181, 182]. Wide-angle x-ray diffractions (up to approximately 15 Å repeating units) of unstretched human hair and other keratin fibers (wool and porcupine quill) show several related spacings, among which are an equatorial spacing (perpendicular to

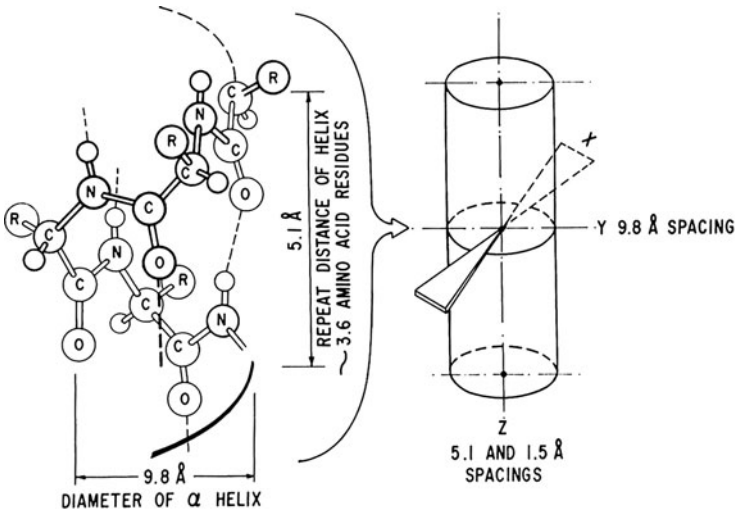

Fig. 1.37 Structure of an alpha-helix proposed by Pauling and Corey

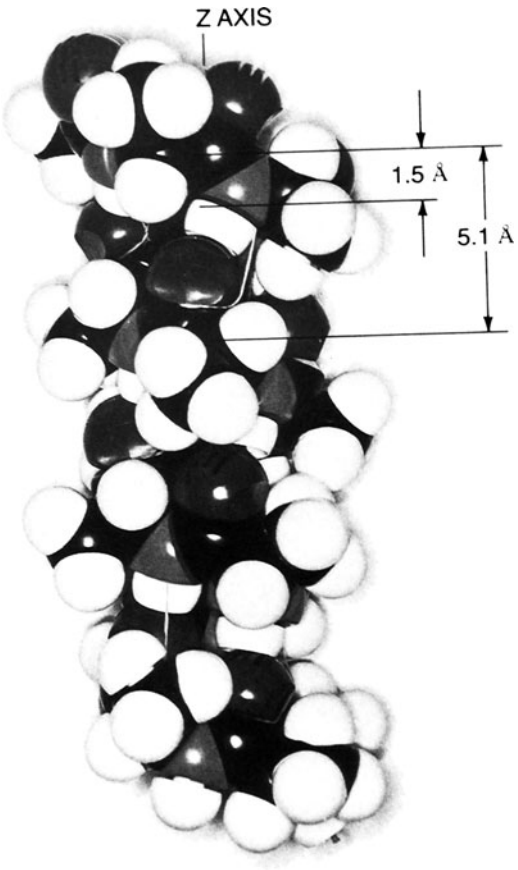

Fig. 1.38 Molecular model of a left-hand helix of polyalanine. A right-hand helix (spiraling in the other direction) is the pattern found in most proteins, including animal hairs (see Fig. 1.37)

the fiber axis) of 9.8 Å and meridional spacings (parallel to the fiber axis) of 5.1 and 1.5 Å (see Figs. 1.37 and 1.38).

Pauling and Corey interpreted the 1.5-Å spacing to represent the distance between each amino acid residue. The 5.1-Å spacing was assigned the repeat distance for coiling; corresponding to 3.6 amino acid residues and the 9.8-Å spacing represented the center-to-center distance between each alpha helix. This latter spacing approximates the thickness of the alpha helix. A linear polypeptide alpha helix would have a repeat distance of 5.4-Å units. Therefore, coiling of each helix [183] was proposed to account for the shorter 5.1 meridional spacing. Furthermore, it was originally suggested that two- or three-strands of polypeptides were coiled about each other analogous to a twisted rope [184–186]. This structure has been routinely referred to as the "coiled coil" model. The model that is now accepted for animal hairs is the two-strand rope polypeptide described in the previous section entitled, *The Intermediate Filaments*.

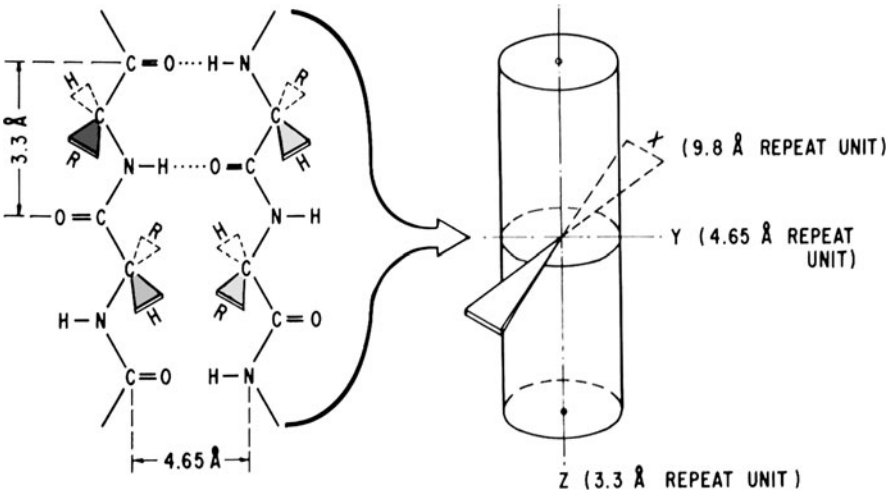

Fig. 1.39 Portions of two polypeptide chains in the beta configuration. The cylinder represents a hair fiber, and the axis identifies the orientation of the proteins in the fiber. See corresponding molecular models in Fig. 1.40

1.8 Stretching Hair and Stress Strain Models

Stretching hair can produce splits or cracks in the endocuticle and the cell membrane complex. Transverse cracks also occur in the cuticle layers as well as damage to the cortex. Nevertheless prior to this past decade, most of the scientific attention relating to stretching hair has been concerned with cortical effects; see Chaps. 6 and 9 for details related to damaging effects by stretching hair.

Astbury [179] found that water produces negligible effects to the wide-angle x-ray diagram of keratin fibers. However, extension in water diminishes the intensities of the reflections corresponding to the α helix and produces a pattern called β keratin represented by a 3.3-Å reflection along the fiber axis (the Z axis in Fig. 1.39), a 4.65-Å reflection at right angles to the Z axis (along the Y axis), and a 9.8-Å reflection at right angles to the Z axis (along the X axis) [167]. The molecular model of Fig. 1.40 describes the interpretation of these reflections in terms of molecular structure. Most explanations of this phenomenon invoke an α to β transformation, that is the transformation of molecules of the α-helical structure into the pleated sheet arrangement of the β structure.

To explain the stretching behavior of hair, many scientists consider hair consisting of only two components, IFs and matrix; however, to explain the fracture behavior of hair we must also involve the cell membrane complex. Some swelling models also consider only the intermediate filaments and matrix; however, Swift [187] provided some consideration to the non-keratin components for explaining the swelling behavior of keratin fibers. See the next section entitled *Swelling Behavior of Hair*.

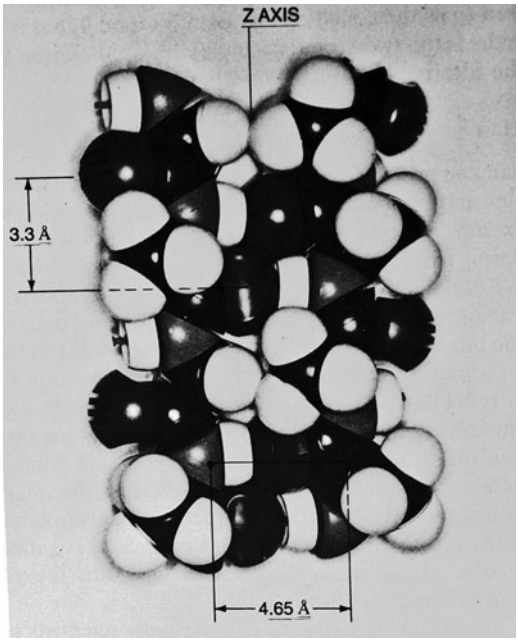

Fig. 1.40 Molecular model of two polyalanine chains in the beta configuration

To refine our understanding of the mechanical properties of keratin fibers, models involving the intermediate filament-matrix level of structural organization have been employed by Feughelman [188–190], Bendit [191], Hearle [192], Chapman [193], Wortmann and Zahn [194], and Kreplak et al. [195] and others. Only three of these models will be described along with some more recent relevant work.

1.8.1 Feughelman's Two Phase Model

Feughelman [189, 196] nearly 50 years ago proposed a two phase model in the cortex of animal hairs involving a relationship between mechanical properties and molecular configuration. At about the same time, Bendit [191] considered the α to β transformation to explain part of the stress strain curve of animal hairs. Feughelman's two phase model [188] consisted of water-impenetrable rods (IFs) oriented parallel with the fiber axis embedded in a water-penetrable matrix. This two-phase model is useful for helping to explain the mechanical properties of virgin keratin fibers including extension, bending, and torsional properties and also the swelling behavior of unmodified keratins. Feughelman explained the initial part of the stress strain curve, which is the "Hookean" region, by suggesting that the alpha helices of the IFs are strained, and hydrogen bonds of the globular proteins of the matrix are involved. Feughelman suggested that upon further extension into the

yield and postyield regions, the α to β transformation occurs in the coiled proteins of the IFs producing a loss of helical structure, which is recovered on relaxation.

Feughelman's model explained that the globular proteins of the matrix act in parallel with the IFs. The matrix phase is weakened by the presence of water. On the other hand, the crystalline regions of the IFs are virtually inert to water over the entire load-extension curve. In 1994, Feughelman modified and updated his model to what is called an X/Y zones model [190]. For additional details of the extension behavior of keratin fibers see the remaining discussion in this Chapter and Chap. 9 and for effects of extension on the cuticle see Chaps. 6 and 9.

1.8.2 Wortmann and Zahn's Model

Wortmann and Zahn [194] in 1994, proposed a different model placing more emphasis on the structures of the IFs and less emphasis on the matrix which they considered a gel to sol system. These scientists suggested that the opening up of two different parts of the IF monomer is responsible for the yield and post yield parts of the stress strain curve. Furthermore the increased slope in the post yield area is due to the sulfur bonds in one of the monomer segments of the IFs and that disulfide-sulfhydryl interchange occurs in the post yield region.

This model by Wortmann and Zahn [194] does seem to address many of the concerns of others [195, 197, 198]. For example, Wortmann and Zahn calculated that about 20% of α helices have opened up at the end of the yield region [27, 31]. Furthermore, they suggested that 48–56% of the α helical material has been converted to β segments upon the breaking stress in water (60–70%) strain. These calculations by Wortmann and Zahn are consistent with the findings of Kreplak [195].

The structural model by Wortmann and Zahn [194] places less emphasis on the matrix proteins and explains the fiber tensile behavior in terms of the molecular structure of the IFs and bonding within and to these important structures. This model suggests that the yield region arises by the α-helical chains uncoiling because they are not restricted by disulfide bonds. In this model the post yield region occurs in the domains restricted by disulfide bonding and the disulfide bonds continue to inhibit stretching until the fiber breaks. However, even this model fails to explain the stress.strain behavior of chemically oxidized or sun oxidized keratin fibers.

1.8.3 Other Models/Modifications and Some Concerns

More recently, slight modifications or neuances to the above models (or a new model as suggested by the authors) were proposed by Kreplak et al. [195] with supporting evidence by small-angle x-ray scattering on stretched α-keratin fibers. Interpretation of the data of these scientists suggested that the mechanical stretching

of hair fibers involves both stretching and sliding of keratin molecules inside the IFs. Furthermore, the water content of the fibers determines the relative importance of sliding vs. stretching. For example, when stretching hair fibers in water, the molecular sliding process is dominant up to about 40% strain where it is believed that stretching becomes more important. However, at 45% RH both stretching and sliding occur and the end result is unfolding of the α-helices to β-sheets as originally proposed by Bendit [191].

Two papers by Cao [197, 198] provided additional information to consider with respect to these structural models. In the first paper, Cao [197] emphasized that the assumption of a one to one micro.macro (molecular to fiber) relationship has been made by most structural models for explaining the stress.strain behavior of keratin fibers. Cao suggested that the macroscopic 40% extension of the fiber is not actually matched by 40% extension of polypeptide chains throughout the fiber, but intermolecular slippage can occur that can cause rearrangement of the lattice structure.

Cao examined hair and wool fiber using x-ray analysis examining the 5.1 meridional fraction characteristic of the α-form and the 4.65 equatorial diffraction characteristic of the β-form. Cao concluded that a 40% stretch of wet hair that is held at 40% elongation does not display any evidence of a β-form, but only α-form crystallites, however the same 40% stretch followed by steam setting for 20 min shows a β-form crystalline pattern. So, Cao concluded that the α to β transition occurs only while a stretched hair or wool fiber is being set using steam, not while it is being stretched. To my knowledge no one in this field has either addressed, found or reproduced this finding by Cao.

In Cao's second paper on this subject [198], he demonstrated irregular multiple necking or narrowing deformations along the length of the hairs rather than a continuously uniform elongation along the length of the fibers. Cao drew an analogy to the same phenomenon that occurs in the stretching of synthetic polymers. X-ray analysis showed β-crystallinity in the necked sections and α-crystallinity in the non-deformed un-necked sections of the fibers. Furthermore, the greater the percentage of stretching the more β-crystalline form resulted.

Kreplak et al. [199] in a more recent publication sheds additional light on the stretching behavior of horse hair fibers. These scientists showed by wide angle x-ray scattering and high spatial resolution infrared microspectroscopy that the α to β transformation occurs near 20% strain for wet hair and not before. This is close to the end of the yield region, not near the beginning such as 5% strain as suggested by earlier investigators. The data is consistent with the unfolding of α helical coiled coils below 20% but not transitioning to the β confirmation until above 20% strain. Kreplak et al. [199] also suggested that their data is consistent with the α to β transition occurring from 20% to 50% strain and that the transformation occurs first in the fiber core and then moves slowly to the fiber periphery. They suggested that this transition from the fiber core to the periphery is related to differences in crystallinity (the IFs) in the fiber core vs. the periphery.

These experiments by Kerplak et al. were with horse hair, a very straight hair fiber. But we know that there are different crystalline distributions between straight hair and highly coiled hair fibers. For example, both straight human hair and wool

fiber have been shown to possess an annular type cortex with para type cortical cells in the core, meso type cells in between and orthocortical type cells at the periphery of the cortex [150, 151]. On the other hand, highly curled hairs have been shown to contain a bilateral type cortex with more para type cells in the concave side of the curl and ortho type cells in the convex side. Therefore, with Kreplak's model, I would anticipate that stretching straight hairs of all types would originate first in the core and move to the periphery as found by Kerplak et al. [199]. However, for highly curled hairs, I would conclude that the alpha to beta transition would first begin in the most concave side of curls and then move to the other side.

1.8.4 Fractographic and Damaged Hair Concerns with These Models

To explain the load elongation behavior of the most virgin parts of the fibers these models appear to be reasonably sufficient. However, to explain load elongation behavior up to and including catastrophic failure for certain types of hair damage, these models do not explain fractographic results and consequences of certain types of hair fiber damage. For example, as hair is damaged especially by free radical oxidative treatments fractures are propagated along the axis through the cell membrane complex [200, 201] and the medulla [200] providing step fractures, fibrillated ends and split hairs [200, 201]. Feughelman [202] in his book explained that the stronger cortical cells dominate the bulk properties of the cortex until the CMC fails. He stated further that the CMC does not have "any effect on the measurement of the mechanical properties of the cortex until failure is approached." Furthermore, he did not describe any instances where damage occurs to the CMC or produces effects on the mechanical properties.

Fractures can occur in the CMC before catastrophic failure in hair fibers on live heads with sunlight exposure and/or normal oxidative cosmetic treatments and on African hair with twists. I arranged with a local hair dresser to collect hair clippings from a few of his selected customers; those he believed to have split hairs. A questionnaire was devised and completed by the hair dresser in collaboration with the customer on the type of hair and the different treatments and conditions that the hair had been exposed to. Hair cuttings were collected from eight female Caucasians. Prior to cutting, all hair samples measured approximately 35–55 cm long and the amount of hair cuttings varied from a total of 2–12 g. A total of 272 split hairs were found and classified into six different types of splits. The highest frequency and most severe splits were from four panelists who frequently treated or exposed their hair to peroxide-persulfate or to two or more of these products/exposures known to involve free radicals: peroxide-persulfate, sun bathing, oxidation dyes and hot irons (straightening or curling). From these hairs, several examples were found indicative of CMC fracturing before catastrophic failure. Two of these

examples will be described and several are illustrated in Chap. 10 in the section entitled, *Split Ends, Types, and their Occurrence & Formation*:

- Split hairs NOT Split ends. This type of split can occur as far as 4 cm from the tip end, and it occurs before catastrophic failure.
- Broom type effects resulting from fractures in the CMC several cm from the tip end. This effect is caused by oxidative cosmetic damage and grooming actions and is analogous to the fractures at the nodes of the hair abnormality in trichorrhexis nodosa. This type of effect occurs before catastrophic failure. These effects illustrate that fractures can occur in the CMC before catastrophic failure and they should produce changes in the tensile curves in some cases prior to the post yield region. However, if such effects are observed in testing, the data could lead to premature failure for some fibers and will often be omitted as outliers. So, hairs that have been exposed to free radical cosmetics and/or sunlight and taken directly from live heads can have extensive damage to the CMC. Therefore, I conclude that hairs treated similarly but fractured less extensively in the CMC should produce some detectable changes in their mechanical behavior prior to catastrophic failure.

Kamath and Weigmann [200] determined that more smooth fractures are formed than axial fractures at high humidity or in the wet state. Furthermore, at high humidity or the wet state crack initiation tends to be near the cuticle-cortex boundary, and then the crack propagates toward the center of the cortex [200]. Kamath and Weigmann concluded that when the hair is wet or at high humidity the swelling pressure of the cortex on the cuticle is involved in crack initiation. In addition, more axial splitting was obtained from hair fibers in which the cuticle had been damaged and partially removed by abrasion than non-abraded hair permitting Kamath and Weigmann to conclude that a strong intact cuticle inhibits axial splitting of hair fibers [6].

Robbins [203] in his review of the CMC described its sensitivity to free radical reactions as demonstrated for both human hair and wool fiber and that this sensitivity leads to an increase in step fractures, split hairs and fibrillated ends.

Brown and Swift [201] tested root sections and weathered tips of long (more than 50 cm) human hair fibers from six Caucasian females in a tensile tester at room humidity and temperature. These scientists observed more smooth fractures in the root sections and more longitudinal and circumferential splitting (axial fracturing) in the more weathered tip ends.

The stress.strain models (described above) do explain load elongation in the Hookean and yield regions for virgin hair, but they are less effective in the post yield region particularly in damaged hair when fractographic studies and other evidence suggest that the CMC is involved [200, 201].

For example, undamaged virgin hair roots generally provides a smooth fracture in water, usually beginning near the cuticle-cortex boundary [200] (in the post yield region) and it continues across cortical proteins and appears to be consistent with the stress.strain models. However, for sun damaged hair or highly weathered tip ends, the CMC can be sufficiently damaged primarily by free radical oxidation to

weaken the cortex CMC [203] and with it the cell membrane proteins; so axial fracturing occurs and the CMC is involved.

In this case, a fracture may begin in the cortical proteins in the post yield region as suggested by either the Feughelman model (in the amorphous proteins) or the Wortmann-Zahn model (in the intermediate filaments). After the crack has propagated to where it encounters the weakened cell membrane complex it is diverted and propagated through the CMC and the medulla (if present) and then diverts once again to another region of the cortical proteins to provide a step fracture. On the other hand, if the CMC is extensively damaged, once the crack first diverts into the CMC it can spread in the CMC to provide a split hair or a fibrillated end depending on how badly the CMC has been damaged. So, to explain the stress.strain behavior of these types of damaged hair fibers the intercellular regions of the hair fiber must also be involved.

If we have a hypothesis or a model that explains the tensile properties of undamaged virgin hair, but it does not explain the stress.strain behavior of many common types of hair damage or even damage to the weathered tip ends of hair and African type hair, it is of limited value. So, to increase the value of these models they should be extended to explain common forms of hair damage in addition to simply explaining undamaged virgin hair. It would appear that the weakest links in "virgin" hair fibers to tensile extension are the structures inside cortical cells. However, with most types of hair damage, as strain or extension continues to higher levels, fracturing extends to and involves the cell membrane complex by forming step fractures, fibrillated ends or split hairs. Furthermore for catastrophic failure that forms a step fracture to occur a crack inside a cortical cell must extend across and axially through the CMC. Therefore the CMC must be involved in any hypothesis or model to fully explain the tensile properties of hair especially when considering damaged hair fibers.

I conclude with Hearle [192] that we need a better understanding of the molecular organization of what is called the "amorphous" matrix and the keratin associated proteins to better understand the mechanical properties of hair and wool fiber. But, in addition we need a better understanding of the molecular organization of the cell membrane complex too.

1.9 Swelling Behavior of Hair

The organizational level believed to control the swelling behavior of keratins is the secondary and tertiary structure of the IFs and the matrix [204]. As indicated previously, the IFs consist of proteins containing alpha-helical segments embedded in the less organized matrix of high cystine content.

In keratin fibers like human hair and wool fiber, the helical proteins of the IFs are oriented parallel with the axis of the fiber (see Fig. 1.41). The IFs help to maintain the structural integrity of the fibers while most of the volume swelling takes place in the matrix proteins [204, 205]. This is consistent with Feughelman's [188] two-phase model of water-impenetrable rods (IFs) in a water-penetrable matrix. As a

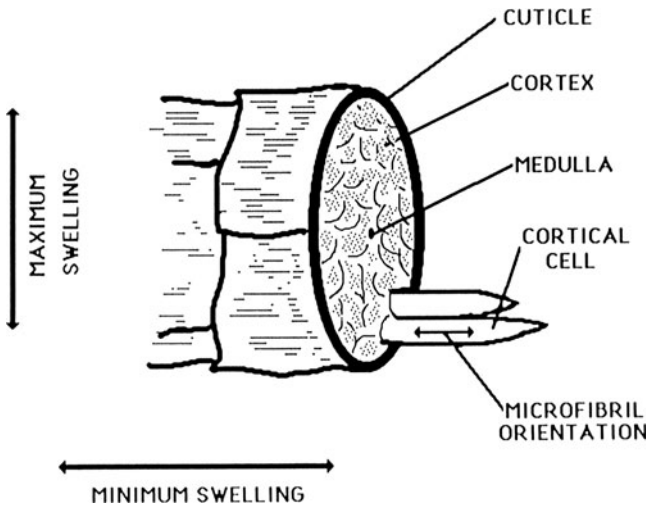

Fig. 1.41 Schematic illustrating the directional swelling of human hair

result, maximum swelling occurs between the IFs and minimum swelling occurs along the axis of the IFs. Therefore, maximum swelling occurs in the diametral dimension of hair, and minimum swelling occurs in the longitudinal dimension that is along the axis of the fibers (see Fig. 1.41). For example, Stam et al. [206] has shown that from 0% to 100% relative humidity, hair increases nearly 14% in diameter, but less than 2% in length. Other reagents such as sodium lauryl sulfate, formic acid, and thioglycolic acid produce more swelling than water but dimensionally they swell hair similarly; that is they produce greater swelling in the diametral dimension than in the fiber length [204].

Swift [187] and others suggested that the non-keratin portions of hair are also important to fiber swelling. For example, Swift demonstrated by the penetration of fluorescent labelled proteins in water that a large order swelling occurs in the non-keratin regions of hair. The diametral swelling of hair by water from the dry state is about 14% to 16%. On the other hand, Spei and Zahn [207] using x-ray diffraction measurement of inter-IF separation distances indicates that swelling of only 5.5% occurs. Swift, therefore, proposed that part of the difference can be explained by swelling that occurs in the non-keratin regions of the cuticle and the cortex. For additional details on swelling of human hair, see Chap. 9.

Protein from the IFs of human hair can be isolated by oxidation with peracetic acid according to the method of Alexander and Earland [159]. One fraction obtained by this procedure is called alpha keratose. See Chap. 2 in the section entitled Other Protein Fractionation Methods. The alpha keratose fraction amounts to about 45% of the fiber mass, containing a substantially lower proportion of sulfur than the other two keratose fractions (see Table 2.16). The low sulfur content suggests a relatively low proportion of the amino acid cystine in the IFs and therefore a low proportion of cystine in the alpha-helical proteins. This conclusion

is consistent with the amino acid analysis of alpha keratose isolated from merino wool by Corfield et al. [160], showing a relatively low percentage of cystine and a high percentage of the other bulky amino acids. This keratose fraction is in all probability not purely IF in origin and likewise not pure alpha-helical protein. However, the fact that it can produce an x-ray pattern similar to that of alpha keratin [159], and the other two-keratose fractions cannot, suggest that its origin is the IFs.

1.10 The Origin of Hair Fiber Curvature

We frequently refer to hair fibers as being round, however most hair fibers are actually oval shaped. In addition, many hairs defy a single word or measurement for their cross-sectional shape because they are often twisted and indented with very irregular cross-section and surface appearances; see Chap. 9 for a more complete discussion of hair fiber shape including illustrative micrographs of hair fibers.

More than 40 years ago, Mercer [208] proposed that the shape of hair fibers is determined by the shape of the hair follicles in the zone of keratinization. Lindelof et al. [209] concluded from 3-D computer-aided reconstruction of serial sections of human hair follicles from ten patients of three biological races that the shape of the follicle is a primary factor in determining the final hair form or shape. For example, Lindelof et al. reported that the African follicle had a helical form, while the Asian follicle was essentially straight and the follicle of Caucasians varied between these two extremes.

Orwin [210] found that breeds of sheep that bear fine-wool tend to have follicles of narrower diameters and longer follicles correlate with longer wool fibers. These facts suggest that the size and shape of the follicle could play a role in the final shape of hair fibers and that the growing fiber takes the shape of the mold where hardening or keratinization occurs. Thus, if the follicle or sac that the fiber is formed in is highly curved in the zone of keratinization, the emerging hair fiber should be highly curled, but, if the follicle is relatively straight, the emerging hair will be straight. This mechanism to explain hair fiber curvature is analogous to the shape that is formed for an extruded monofilament for synthetic polymers.

An alternative explanation considers the bilateral structure of some keratin fibers like wool. A helical fiber will arise if opposite halves of the fiber grow at different rates or if opposite halves contract to different extents during drying or with moisture changes. This conclusion is analogous to the way a bilateral thermostat bends with changes in temperature and considers protein composition and distribution as important factors for fiber shape.

In the 1950s Mercer [211] and Rogers [212] independently identified two types of cortical cells in merino wool fibers. These two types of cells were named orthocortex and paracortex (see Fig. 1.32). Later, Kaplin and Whiteley [213] were able to distinguish between three different types of cortical cells in high-crimp and low-crimp merino wool. Cells on one side of the cross section contained

whorls of IFs. These were called orthocortical cells, while the names paracortical cells and mesocortical cells were used for those cells without whorls of microfibrils that were arranged opposite to the orthocortical cells in wool fibers of high crimp and low crimp, respectively [214, 215].

Highly crimped wool fibers like merino wool, camel, vicuna and guanaco hair have all been shown to contain bilateral cortical structures with nearly an equal amount of ortho-cortical and para-cortical cells [215, 216]. On the other hand, non-bilateral structures have been described for relatively straight animal hairs such as mohair and alpaca [215].

In 1972 Leon [148] described both orthocortical and paracortical cells for Negro hair with a "higher proportion of ortho type cortical cells than for Caucasian hair". Swift [149] more recently reported that highly twisted hair from a Black man from Nigeria was asymmetrically divided and contained about 50% paracortical and 50% orthocortical cells. On the other hand, straight hair from Japanese contained only para-cortical cells and thus did not contain bilateral structures of ortho and paracortical cells. For curly Caucasian hair, Swift observed mostly paracortex with a layer of only one cell thickness of orthocortical cells at the periphery of the cortex, but not a bilateral structure.

Horio and Kondo [217] found in fine high crimp wool fibers that the bilateral arrangement of ortho- and paracortical cells occurs with the orthocortex on the outside of the curve or curl and the paracortex on the inside of the curl. This arrangement was confirmed by Fraser and Rogers [218].

Campbell et al. [219] described the effects of diet on the shape of wool fibers. Campbell worked with two types of sheep, sheep that provided high crimp wool and sheep that provided low crimp wool. These scientists demonstrated that when both groups of sheep were placed on a low nutrition diet, the number of crimps/cm of wool increased see Table 1.17. However, when these same sheep were placed back on the normal nutrition diet the number of crimps/cm of wool decreased once again see Table 1.17.

Campbell explained these results by suggesting that wool fibers produced on a low nutrition level moves more slowly through the follicle than fibers produced at a normal nutrition level. Furthermore, curved follicles with a faster growth rate should move the soft unhardened fiber through the zone of keratinization faster and the faster the fiber moves through the zone of hardening the fewer crimps produced. But, an alternative explanation is that on a low nutrition diet sheep are not capable of producing the required amount of the specific proteins that are

Table 1.17 The effect of nutritional levels in sheep on wool fiber crimp, from Campbell et al. [219]

	High crimp wool			Low crimp wool		
Nutrition level	Normal	Low	Normal	Normal	Low	Normal
Crimps/cm	7.0	9.0	6.7	1.7	3.8	2.0
% S	4.08	3.17	4.08	3.26	2.75	3.22
% High S protein	32	22	29	24	17	20

necessary for producing the required bilateral content for a high degree of crimp and curl, i.e., specific IF or KAP proteins. Note, the percentage of high sulfur proteins also decreased and increased with the crimp, see Table 1.17. This effect of producing less high sulfur proteins would produce a lower paracortical cell content resulting in less bilateral content and therefore less crimp or curl.

1.10.1 Structures in the Cortex Associated with Curvature

The cortical cells of human hair are composed of fibrillar components called macrofibrils that are connected by inter-macrofibrillar material, cytoplasmic remnant and melanin granules. The macrofibrils consist primarily of filamentous proteins that form IF's that are held together laterally and in orientation by amorphous type proteins called keratin associated proteins (KAP's). It has been shown that the distribution of different cortical cell types with their corresponding IF arrangements are related to hair fiber curvature in wool, camel, alpaca and mohair fiber [215–217] and in human hair fibers [150, 151].

Thibaut and coworkers [150] studied hair from six persons of Caucasian, North African and African descent. This hair was described as straight (Curl type I), wavy (Curl type II or III) and curly human hair (Curl types IV–VII). These STAM (Chap. 9) curvature types are based on my estimates from the photographs in the Thibaut et al. paper. Thibaut et al. found evidence for three types of cells in the cortex of these hairs. These scientists indicated that the cell types were similar to the orthocortical, mesocortical and paracortical cells found in wool fiber [217, 218, 220, 221]. In straight hairs, a core of paracortical type cells were generally surrounded by mesocortical and orthocortical type cells in an annular type arrangement.

The amount of mesocortical type cells decreased with increasing fiber curvature. Only orthocortical and paracortical type cells were identified in tightly coiled African hair and these were distributed asymmetrically with the orthocortical type cells predominately on the convex side of the curl and the paracortical type cells on the concave side, see Figs. 1.32 and 1.42.

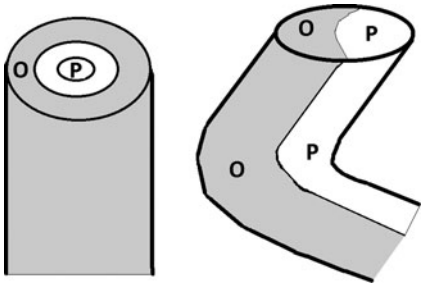

Fig. 1.42 Schematic of a straight and a curled hair illustrating orthocortex type and paracortex type distributions in the fiber

Thibaut et al. [150] indicated that the distribution of the keratin protein hHa8 (a building block of specific IF's) was found to be associated with the amount of curliness. As the degree of curvature increased the amount of hHa8 keratin accumulated more to the concave side of the curl. In tightly curled hair it was almost exclusively on the concave side along the length of the fiber [150]. Since hHa8 keratin is a component of IF protein and its location in the fiber cross-section is curvature dependent one can conclude that the organization and likely the orientation of the IFs are most likely related to hair fiber curvature.

Kajiura et al. [222] studied a wide range of hair fiber curvatures (Curl types I, III, IV, and V–VIII, which I classified from the curl radii provided) of human hair (African American, Asian and Caucasian) and wool fiber by small angle x-ray scattering (SAXS). These scientists found that the gap between IFs is larger on the concave side of a curl in human hair and smaller on the convex side. This suggests more matrix material between IFs on the concave side of a curl in human hair and is consistent with the observation in wool fiber of more paracortex (more matrix material than orthocortex) on the concave side of a curl or curve and more orthocortex on the convex side of a curl [218, 221], see Table 1.18 and Figs. 1.32 and 1.42.

Bryson et al. [151] examined hair fiber curvatures from Curl type I, III and IV of Japanese hair (I calculated STAM Curl types from curl diameters in that paper) and they described four different types of cortical cells. These scientists labeled these cell types as A, B, C and D and found all four cell types in straight and curved hairs. The cells were more symmetrically distributed in straight hairs consisting mainly of annular bands of cell types around the center of the fiber analogous to the arrangements in straight Caucasian and Asian type hair [150].

Curved hairs (Curl type IV) in fluorescent stained and TEM hair sections showed strong bilateral symmetry with respect to the distribution of cell types with mainly B type cells and some C or D type on the convex side and primarily C type with a

Table 1.18 Some properties of orthcortical and paracortical type cells in keratin fibers

Orthocortical B or D[a] cells	Paracortical and C[a] cells
On convex side of curl [151, 212, 218]	On concave side of curl [212, 218]
Lower: Matrix/IF's [222–224]	Higher: Matrix/IF's [222–224]
More crystalline	Less crystalline
IF's: Helical whorl-like [151, 220]	IF's: Parallel arrays [220][b]
Less cystine rich proteins [225][228][c] fewer cross-links	More cystine rich proteins [225][228][c] more cross-links
Lower sulfur content [227]	Higher sulfur content [227]
Acidic: Binds more Cationic dyes	Basic: Binds more anionic dyes
More extensible and flexible [151]	Less extensible and flexible [151]
Lower water binding (all RH's)[d]	Higher water binding (all RH's)[d]

[a]The properties of this table have been demonstrated for orthocortical and paracortical cells in wool and I conclude they are directionally similar for B and C cells in hair
[b]Bryson et al. [151] show C cells more of a hybrid between ortho- and paracortical
[c]Shown concave vs. convex side of curl and assumed to be in cell types as indicated
[d]I conclude these effects for water absorption based on crystalline (IF) content.

few B type cells on the concave side similar to the findings of Thibaut et al. [150] who called the cells types ortho-, meso-, and paracortical types.

Table 1.18 describes some important properties of orthocortical and paracortical cells in wool fiber. These properties are assumed to generally (but not entirely) correspond to the properties of B type and C type cortical cells in human hair respectively.

Bryson et al. [151] suggested that the cortical cell types of wool fiber are easier to differentiate and are more distinctly separated bilaterally than in high curvature Japanese hair. These scientists [151] also suggested that type B cells of human hair are similar but not exactly the same structurally to orthocortical cells of wool fiber see Table 1.18. The macrofibrils of type B cells contain "helical/whorl-like IF arrangements" similar to orthocortical cells [151]. Type C cells although similar structurally to paracortical cells of wool fiber are more of a hybrid between orthocortical and paracortical cells with respect to their arrangement of IF's [151]. The macrofibrils of type C cells contain IF's in both "helical/whorl-like" arrangements and "parallel arrays" [151].

The type B cells of Japanese hair [151] and orthocortical cells of wool fiber [212, 218] are primarily in the convex side of fiber curls while the type C cells of Japanese hair [151] and paracortical cells in wool fiber [212, 218] are largely in the concave side of curls. The orthocortical cells [223, 224] and the B cells (on the convex side of curls) contain more IF material [151, 223, 224], less matrix [151, 224, 226] and a lower cross-link density [225] and therefore are believed to be more flexible and more extensible than paracortical cells [151] or C type cells [151] on the concave side of curls.

Bryson et al. [151] suggested when hair or wool fiber is wet with water and dries out the convex fiber side (less cystine, therefore more extensible and flexible) should extend more longitudinally than the concave fiber side causing the fiber to bend toward the region of highest type C cell or paracortical cell concentration. This suggestion is consistent with the cystine composition of these different cell types, see Table 1.18.

Thibaut et al. in another publication [228] provided an explanation for this type of asymmetric cell production and growth by demonstrating that in curly follicles, both the outer root sheath (ORS) and the connective tissue sheath lack symmetry along the follicle. Where the follicle is convex, the ORS is not as thick and the rate of differentiation by the inner root sheath is decreased. Therefore, these scientists concluded that an asymmetric distribution of proteins in curved hair follicles relates to and is controlled by this lack of symmetry in the ORS and connective tissue sheath around the follicle.

Furthermore, Thibaut et al. [228] demonstrated that when curly hair fibers (African or Caucasian) are dissected and removed from the scalp biopsy and the lower part of the hair follicle placed in in-vitro media the curvature of the emerging fiber appears to be retained as if it were growing in the follicle. From these experiments these scientists concluded that hair curl is "programmed from the bulb" and is related to or controlled by "asymmetric differentiation" as the fiber moves up the follicle.

I conclude that the primary factor controlling hair fiber curvature is programmed from the bulb by the symmetry of protein distribution. However, whether hair follicle shape in the zone of keratinization affects hair fiber curvature in some way analogous to the production of a synthetic filament as it is extruded or whether curvature is controlled entirely by programming from the bulb by the symmetry of the distribution of proteins in the final fiber awaits further research.

1.11 The Structure of the Cell Membrane Complex

The cell membrane complex (CMC) consists of cell membranes and adhesive material that binds or "glues" the cuticle and cortical cells together in keratin fibers. G.E. Rogers from his seminal high resolution transmission electron microscope (TEM) studies of animal hairs provided evidence for the general structure of the CMC. The CMC consists of a central Delta layer approximately 15 nm thick sandwiched by two lipid layers called Beta layers each in the vicinity of 5 nm thick [212, 229], see Fig. 1.26 adapted from Fraser, MacRae and Rogers [223]. Jones et al. [230] described the uncertainty of the composition of the Delta layer because of the difficulty of isolating it without changing it.

Questions still exist about the relative thickness and composition of the Beta layers between cuticle cells vs. the Beta layers of cortical cells (see Figs. 1.43, 1.44 and 1.45) and between the upper Beta layer vs. the lower Beta layer of cuticle cells. Although, most authors quote the thicknesses of the Beta layers between 2.5 [114] and 5.0 nm, 6.0 nm has also been cited [130]. In addition the upper Beta layer

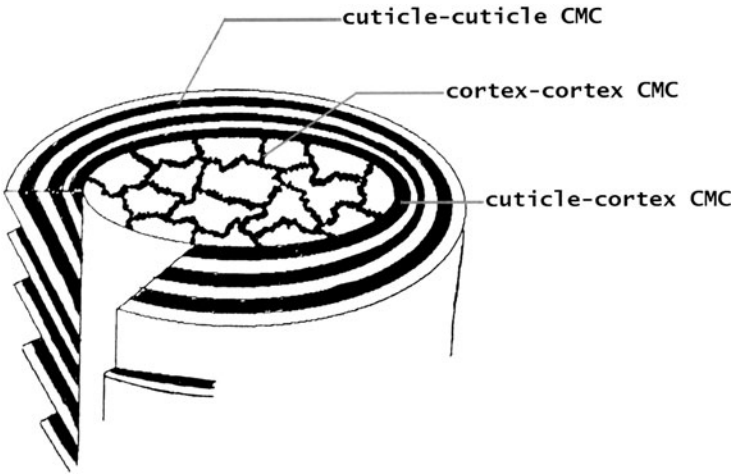

Fig. 1.43 Schematic diagram illustrating the location of the three types of CMC in hair fibers (Reprinted with permission of the Journal of Cosmetic Science [203])

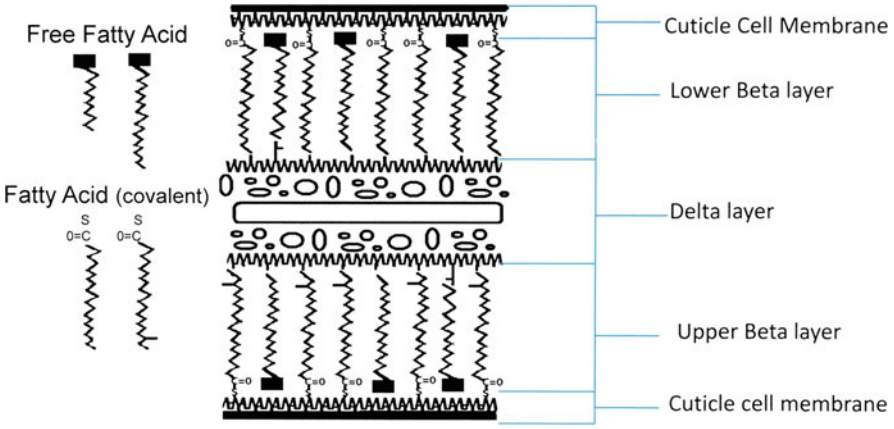

Fig. 1.44 Schematic proposed for the cuticle-cuticle CMC [203] (Reprinted with permission of the Journal of Cosmetic Science)

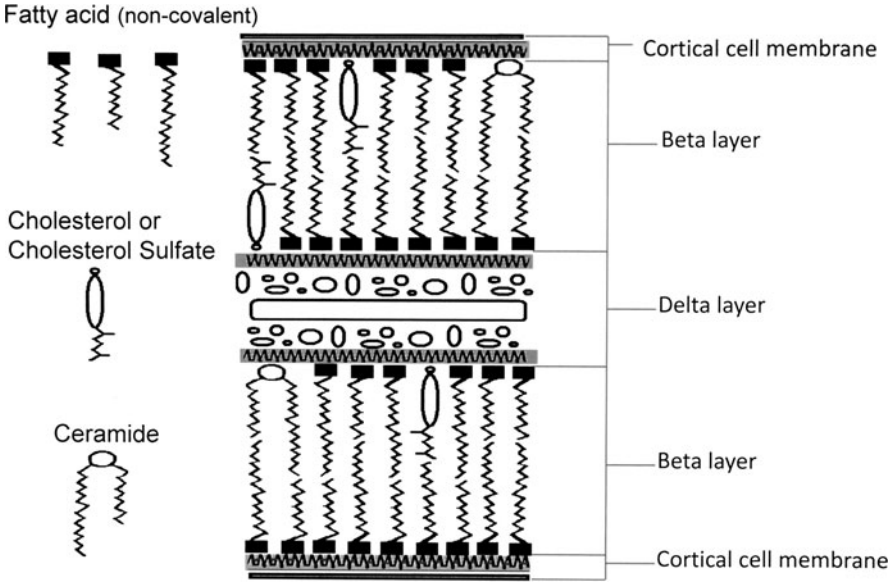

Fig. 1.45 Schematic representing the cortex-cortex CMC [203] (Reprinted with permission of the Journal of Cosmetic Science)

appears to be thicker than the lower Beta layer [229, 231]. Swift [107] in his review of the human hair cuticle described the difficulty of obtaining accurate measurements of the Beta layers in the high resolution TEM. Swift's explanation clarifies the uncertainty that exists in ascribing mono-layers or bi-layers to these lipid strata on the basis of TEM measurements alone. From his TEM studies, Swift

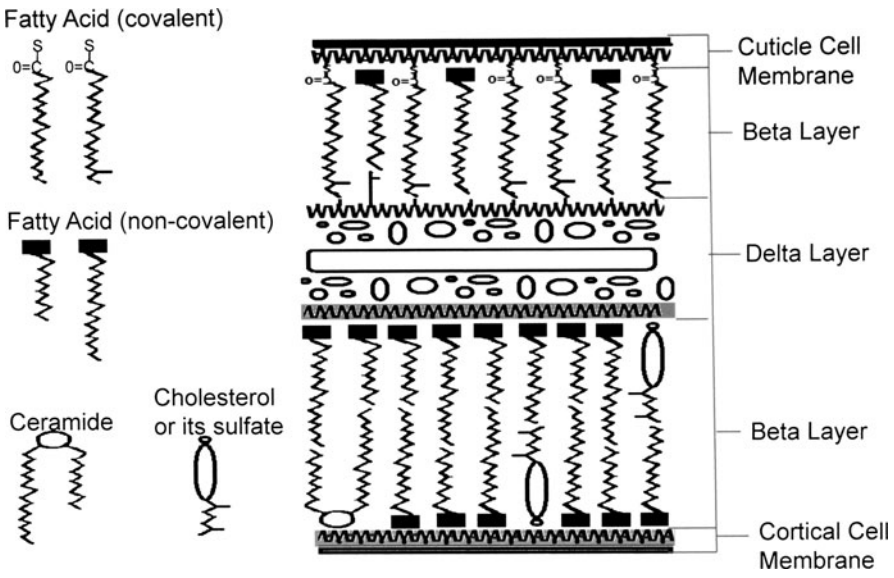

Fig. 1.46 Schematic representing the cuticle-cortex CMC [203] (Reprinted with permission of the Journal of Cosmetic Science)

[232] cited 3 nm thicknesses for the cuticle Beta layers. Relatively recent analyses by microbeam diffraction [142, 143] also cite 3 nm thicknesses for these same layers between cuticle cells, see the section entitled, *Thickness of the Cuticle Beta Layers* in this chapter.

Three types of CMC have been described in the literature [233]: cuticle-cuticle CMC representing CMC between cuticle cells, cortex-cortex CMC representing CMC between cortical cells and cuticle-cortex CMC representing CMC at the cuticle cortex boundary see Fig. 1.46. Since Rogers' [212, 229] initial description of the CMC and his additional work demonstrating that the Delta layer of the cortex consists of five sub-layers [223] several additional important developments have occurred that will be described in the next section adding details to this important structure in animal hairs.

1.11.1 General Differences for Cuticle-Cuticle CMC Versus Cortex-Cortex CMC

Jones and Rivett [125, 234] provided evidence that the CMC of the cuticle contains 18-methyl eicosanoic acid (18-MEA) in its upper Beta layer. 18-MEA has never been shown to be in the CMC of the cortex. The facts strongly suggest that the CMC of the cuticle has monolayer lipids that are attached by covalent bonds (primarily thioester) [122, 235] with some ester or amide linkages [235] to proteins of the cell

membranes on one end and attachment by van der Waals attractive forces to proteins of the Delta layer on the hydrophobic end of the fatty acids (Fig. 1.44). The evidence shows that the CMC between cortical cells consists of lipid bi-layers that are not attached by covalent bonding to protein layers. The lipid bi-layers of the cortex are bound by salt linkages and polar bonding to the cortical cell membrane proteins on one side and similarly attached to the Delta layer on the other side of the bi-layer, see Fig. 1.45.

1.11.2 The Cuticle-Cuticle CMC

In 1916 Allworden [126] discovered that Chlorine water reacts with the cuticle cells of wool fiber to produce large bulbous sacs on the fiber surface. Chlorine water degrades proteins beneath the cuticle cell membranes, (most likely cleaving and oxidizing disulfide bonds between the epicuticle and the A-Layer [236]) producing water soluble species too large to diffuse out of the semi-permeable cuticle cell membrane. Swelling results from osmotic forces and the cuticle membrane stretches producing the Allworden sacs (Fig. 1.29) that separate from the underlying proteinaceous cell layers.

The epicuticle membrane was first isolated and named by Lindberg et al. in 1949 [237, 238]. Nineteen years later, Leeder and Bradbury [100] defined the epicuticle as the "thin outer membrane which is raised on the surface of fibers as sacs by treatment with chlorine water" in the Allworden reaction. The epicuticle (uppermost cuticle cell membrane) provides the supporting structure for fatty acids in the cuticle, see Fig. 1.44. It is also attached to the A-layer of cuticle cells of wool and human hair and together with 18-MEA is perhaps the most thoroughly studied part of the CMC. Leeder and Rippon [239] in 1985, suggested that the epicuticle was proteinaceous and covered with a strongly bound lipid layer that could not be removed by lipid solvents, but could be removed with alcoholic alkali. They called this covalently bound lipid layer the F-layer.

The F layer together with the cuticle cell membranes (essentially the epicuticle) is analogous to the cornified envelopes or the cellular envelope of stratum corneum. In 1945, Weitkamp [240] reported 18-MEA in wool wax (degras). Forty years later, in 1985, Evans et al. [241] demonstrated that 18-MEA is covalently bonded to the keratin fiber surface by reacting wool fiber with anhydrous alkali after solvent extractable lipids had been removed. The cleavage of 18-MEA with chlorine water by Negri et al. [122] and by hydroxyl amine at neutral pH by Evans and Lanczki [235] support its attachment by a thioester linkage rather than an ester or amide link. In addition, Evans and Lanczki [235] and Korner and G. Wortmann [242] provided evidence for ester and/or amide attachment of some fatty acids (primarily palmitic, stearic, oleic and others) mainly in the lower beta layer on the bottom of cuticle cells.

Jones et al. [243] demonstrated that essentially all of the 18-MEA is in the upper Beta layer of the cuticle-cuticle CMC. Maple syrup urine disease (MSUD) is a

genetic defect in humans and Poll Herford cattle [244] involving 18-MEA. MSUD is caused by a deficiency in the enzyme involved in the synthesis of 18-MEA. Isoleucine is a precursor in the biosynthesis of 18-MEA (an anteiso-fatty acid), involving the branched chain 2-oxo acid dehydrogenase, the enzyme that is deficient in this genetic defect [234]. Anteiso- fatty acids in skin are synthesized from the amino acid, isoleucine [245]. Jones and Rivett in their TEM studies of MSUD [234, 243] found that the structural defect of MSUD in human hair occurs only on the upper surface of cuticle cells (upper Beta layer) where 18-MEA is replaced by straight chain C18 and C20 fatty acids. But, the undersides of cuticle cells (lower Beta layer) are not affected in MSUD. These facts confirm that 18-MEA is attached to the top surface of cuticle cells (upper Beta layer) and not to the underside.

The proteins in the cuticle cell membranes are described in detail in this Chapter in the section entitled *Epicuticle and the Hair Fiber Surface*. In 1993, Negri et al. [122] proposed a model for the keratin fiber surface consisting of a monolayer of 18-MEA covalently bonded to an ultra high sulfur protein through a thioester linkage. These three scientists proposed this attachment at approximately 1 nm spacings. Furthermore, they suggested that the protein support was in the beta configuration and it might be attached to the Allworden membrane.

Although widely varying estimates of the thickness of the epicuticle have been made from 5 to 14 nm, one of the more recent and reliable estimates is by Swift and Smith [115]. These two scientists examined wool fiber, human hair and several other mammalian hairs using high resolution TEM. They identified that the epicuticle is approximately 13 nm thick and is rich in cystine. Swift's estimate of the epicuticle thickness is consistent with the maximum thickness reported by several other workers [129, 132, 246].

Leeder and Bradbury [100, 247] discovered that the Allworden reaction takes place with isolated cuticle cells from several different animal hairs including wool and human hair fiber, proving that this proteinaceous material completely surrounds each cuticle cell and is not a continuous external membrane on hair fibers. In this important scientific effort, cuticle cells were isolated by shaking animal hairs in formic acid. The isolated cuticle cells were then exposed to chlorine water. Formic acid is known to solubilize some proteins believed to be largely from the delta layer of the cell membrane complex. These effects on hair fibers will be discussed later in the section entitled *Proteins of the CMC*.

In the intact fiber Allworden sacs form over the top of cuticle cells (the exposed surface). Leeder and Bradbury suggested that "the sac always occurs on only one side of the cuticle cell" that is the top of cuticle cells and not the bottom [100, 236, 247]. They explained that this effect occurs because the connecting bonds on the top of cuticle cells are between the epicuticle and the A-layer and therefore are most likely through disulfide cross-links that are vulnerable to chlorine water oxidation [236]. Furthermore, they suggested that the connecting bonds on the underside of cuticle cells are between the membrane and the endocuticle (actually the inner layer, a layer about 10–40 nm thick [107] between the endocuticle and the cell membrane and similar in composition to the exocuticle). The bonding on the

underside of cuticle cells is resistant to chlorine water oxidation [236] and therefore could be amide linkages.

Negri et al. [122] determined that the Allworden reaction is an effect of the membranous proteins around cuticle cells. Furthermore, 18-MEA is not required for the formation of Allworden sacs because the sacs can be produced from cuticle in which 18-MEA has been removed by prior treatment with either methanolic KOH or potassium t-butoxide in t-butanol. Because of the bulky nature of the t-butoxide anion, it removes only covalently bound fatty acid at or near the fiber surface. Furthermore, Negri et al. [122] demonstrated that removal of the covalently bound fatty acid facilitates the formation of Allworden sacs because the rate of formation of the sacs increases with prior removal of the covalently bound 18-MEA.

Zahn et al. [133] proposed from indirect evidence using multiple regression analyses for the amino acids from Allen's Allworden membrane data that loricrin, involucrin and an ultra-high sulfur protein were in the epicuticle. These scientists were relating the cell envelope of keratin fibers to the cell envelope of human stratum corneum and the work of Steinert and Marekov [252], Jarnik et al. [253] and Steven and Steinert [254]. See Table 1.19, describing the amino acid analyses

Table 1.19 Amino acids (in mole%) of Allworden membrane vs. calculated values for Wool CE by Zahn et al. [133] and proteins at one time believed to be part of this membrane

A. Acid	Wool CE	H. Loricrin	H. Involucrin	H. UHSP	H. SPRP	Allworden
Asp	2.7	0.3	2.8	3.4	0	3
Glu	9.8	4.4	45.8	8.2	28	8.6
Thr	2.2	2.2	1.6	10.3	2.4	2.1
Ser	15	22.8	1.6	10.9	0.4	14.3
Tyr	0.2	2.5	0.8	1	0	0
Pro	4	2.9	5.7	9	31.2	4.2
Gly	24.5	46.8	6.7	5	0	23.8
Ala	3.2	1	1.5	1.4	0	3.2
Val	3.5	3.5	3.7	3.8	9.6	5.6
Iso	1.1	1.6	0.4	1.6	0	1.2
Leu	2.4	0	14.6	2.4	1.6	2.9
Trp	0	0.3	0	0	0	
Phe	0.8	2.9	0.6	0.8	0	0.4
His	0.9	0.3	4.7	0.7	0.8	0.2
Lys	5.3	2.2	7.4	3.7	12.8	4.5
Arg	1.7	0	0.7	5.6	0	2.5
Met	0	0	0.9	0	0	0
Cys	22.7	6	0.3	32.2	11.2	21.1
Totals	100	99.7	99.8	100	98	97.6

Wool CE calculated by Zahn et al. [133]
Human loricrin from Hohl et al. [248]
Human involucrin from Eckert and Green [249]
Human SPRP from Marvin et al. [250]
Human UHSP from Tezuka and Takahashi [251]
Allworden membrane from Allen et al. [132]

of these and other important proteins adapted from the paper by Zahn, Wortmann and Hocker.

However, more recently, Rogers and Koike [134] used laser capture microscopy to dissect the cuticle, cortex and inner root sheath of human hair fibers. In this manner, these scientists isolated RNA which was subjected to PCR analysis with specific primers to identify mRNA's encoding the surface proteins. No evidence was found for either loricrin or involucrin in the cuticle cell membrane sections, but evidence was found for KAPs 5 and 10 proteins that were likely cross-linked by both disulfide and isopeptide bonds.

Therefore, the proteins of the cuticle cell membranes are associated with the Allworden reaction [126] and are related to the epicuticle and from the work of Rogers and Koike [134] contain KAP's 5 and 10 ultra high sulfur proteins. Since the attachment of 18-MEA to hair proteins is through thioester linkages and the cuticle cell membrane protein is cross linked by cystine bridges, Negri et al. [122] proposed that the lipid layer must be attached to an ultrahigh sulfur protein (UHSP) that can provide attachment sites at approximately 1 nm spacings along the top of its folded chains. This attachment is likely to the KAP's 5 and or 10 proteins.

1.11.3 Bilayers Versus Monolayers in the Cuticle-Cuticle CMC

Whether or not the covalently bound lipids of the cuticle-cuticle CMC are bonded to another lipid layer on their hydrophobic end forming a bi-layer or they are bonded to a hydrophobic protein in the Delta layer is still debated, but this author believes the evidence clearly favors the monolayer model [107, 255] for the following reasons:

- If the Beta layers are mono-layers then 18-MEA is linked to the Delta layer through hydrophobic bonds making the upper Beta layer susceptible to failure at the Delta layer where it has been shown to fail [107, 255–257].
- Swift [107] pointed out that a monolayer model fits better from the point of view of CMC measurements, see the section below entitled, *Thickness of the Cuticle Beta Layers*. Free lipids are very likely in the cuticle Beta layers and the distribution and orientation of these will help determine the thickness of Beta layers.
- If bi-layers exist in the cuticle, there are two options for bonding of the second fatty acid layer to the Delta layer. One is for fatty acids to be covalently bonded to the Delta layer, but this option is not plausible because in human hair and wool fiber 40–50% of the covalently bound fatty acids are 18-MEA [258–260]. Therefore, there are insufficient covalently bound fatty acids in human hair and wool fiber to account for all these fatty acids. The other option is bonding of the second layer of fatty acids through hydrophobic linkages to the covalently bound fatty acids and bonding to the Delta layer through polar and ionic

bonding. However, this type of bonding would provide Beta-Beta failure and not Beta-Delta failure and allow for solvent removal of the non-covalently bound lipid layer which has been shown to occur in cortex-cortex CMC but not in cuticle-cuticle CMC [261, 262]. To provide Beta-delta failure from this bi-layer model, the new hair surface would form a bi-layer consisting primarily of hydrophilic acid groups at the very surface, so this bi-layer model is also not plausible.

- Negri et al. [263] noted that formic acid removes proteins more readily from the cortex-cortex CMC and it modifies CMC junctions of the cortex more than those of the cuticle which is consistent with covalent and hydrophobic bonding of the cuticle-cuticle CMC as shown by the monolayer model of Fig. 1.44, rather than a bi-layer model.

1.11.4 Thickness of the Cuticle Beta Layers

Much confusion exists about the actual thickness of the CMC monolayers as mentioned previously. Swift [232], from a TEM study cited 3 nm thickness for the cuticle Beta layers. Relatively recent analyses by microbeam diffraction [142, 143] also cite 3 nm thicknesses for these same layers between cuticle cells. Part of the confusion about the actual thickness and bi-layers vs. monolayers exists because many consider only the fatty acyl group of 18-MEA as the Beta layer. However, as the following discussion will show that view is not possible.

To measure the thickness of the beta layers Swift [232] used a uranyl acetate/lead citrate stain that stains only carboxylic acid groups. So he measured the unstained part of the TEM images for the Beta layers which he found to be approximately 3.0 nm thick [232]. Thus, only part of Swift's measurement was actually the length of the hydrocarbon portion of 18-MEA fully stretched out (from the thioester group to the end of the hydrocarbon chain which is about 2.39 nm long (for MEA attached at a 90° angle and fully stretched out), see Fig. 1.47. Assuming that the fatty acids of free lipids in between MEA chains are oriented so that the carboxylic acid groups are associating with the thioester groups which is the most stable orientation, then that is where the staining begins on one side because the stain reacts with carboxylic acid groups.

But, 18-MEA is attached to the protein membrane at an angle of approximately 72° (from molecular modeling). So, this angle provides a length of 2.28 nm for the acyl group of 18-MEA alone for the upper Beta layer. Now, since free lipid structures are in between these 18-MEA chains then 18-MEA will be fully stretched out from that angle of 72°.

Now, for the entire unstained part of the Beta layer we must also consider the fatty groups of the Delta layer proteins that the 18-MEA is bonded to all the way to the nearest carboxylic acid side chain; because that is where the staining begins on the other side of this lipid layer. Assuming that this outer protein of the Delta layer is in the Beta configuration and the Van der Waals bonding of 18-MEA is to a

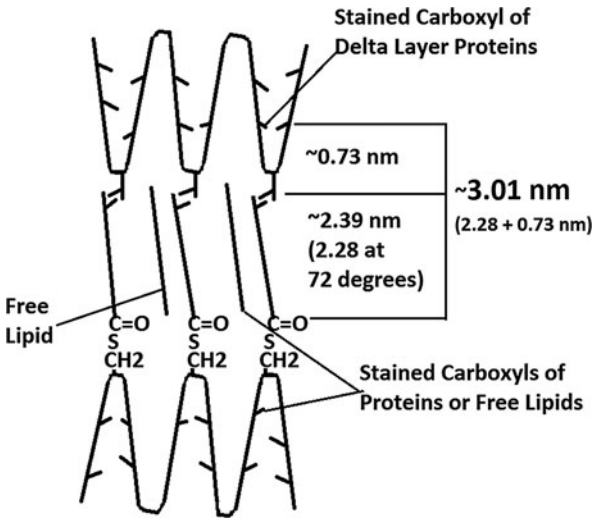

Fig. 1.47 Schematic illustrating the thickness of the cuticle upper Beta layer

hydrocarbon containing amino acid (which it must be), and the nearest amino acid contains a carboxylic acid unit, then this length is approximately an additional 0.73 nm.

Therefore, the hydrocarbon groups of the Delta layer proteins together with the hydrocarbon groups of 18-MEA form what is actually the unstained lipid Beta layer. So, the total calculated thickness of the Beta layer by TEM would be approximately 2.28 + 0.73 = 3.01 nm. Swift [232] found 3.00 nm in excellent agreement. Now if the fatty acid groups are oriented so that their carboxylic groups are near the terminal hydrocarbon end of 18-MEA, then the thickness would be even larger. But, this should be a less stable orientation and not consistent with XPS data showing that the surface of virgin keratin fibers is hydrocarbon-like [125].

1.11.5 Globular Versus Glycoproteins in the CMC

In formic acid extracts, Allen et al. [264] found evidence for glycoproteins in several different animal hairs which they suggested could be from the CMC. However, they suggested that these ingredients might also be remains of cell membrane glycoproteins from the follicle or they could be functional adhesive materials from the CMC. I believe the current evidence favors globular protein in the Delta layer as functional adhesive materials for these reasons:

- The Delta layer resists solubilization by aqueous reducing or oxidizing agents or by acids and alkalies [265]. If the CMC contains globular proteins like many other membranes, then they contain large domains of hydrophobic amino acids on their surfaces [266]. Such a surface is ideal for the hydrophobic ends of the

covalently bound fatty acids to adhere to. Furthermore, this type of globular protein should be resistant to aqueous reagents as Bryson found.

- Bryson et al. in 1995 [265] isolated lipid soluble lipoproteins from the Delta layer of cortex-cortex CMC and not glycoprotein.
- The Delta layer stains with Phosphotungstic acid (PTA). This is either a reaction of hydroxyl groups of a polysaccharide or a primary amine function. Swift [107] explained that this reaction is blocked with dinitrofluorobenzene (DNFB); therefore it is more likely a reaction involving primary amine groups, consistent with a globular protein.
- The Delta layer reacts with periodic acid/silver methenamine [107] a method for polysaccharides, however, Swift [107] also pointed out that since cystine interferes with this reaction, it is still consistent with a globular protein in the Delta layer.

Thus, the globular protein model is consistent with the currently known reactivity of the cuticle-cuticle CMC and the proposed structure of Fig. 1.44. Therefore the glycoproteins that Allen, Ellis and Rivet found were most likely remains of cell membrane material from the follicle.

1.11.6 The Cortex-Cortex CMC

Wertz and Downing [259] found that the percentage of 18-MEA relative to the total amount of covalently bound fatty acids varied from 38% to 48% in five different mammalian hairs including sheep, humans, dog, pig and cow. Table 1.20 summarizes a tabulation of analyses of the covalently bound lipids of wool and human hair from several different laboratories. These results were obtained after the fibers had been exhaustively extracted with chloroform/methanol to remove the non-covalently bound fatty acids and then the residue was saponified with methanolic alkali showing that 18-MEA accounts for about 50% of the covalently bound fatty acids in these wool fibers and about 40% in human hair.

Table 1.20 Covalently bound fatty acids in wool and human hair fiber

	Data for wool fiber					Data for human hair	
Fatty acid	[235]	[267]	[268]	[269]	[242]	Averages	[258]
16:0	8	11	8	17	20	12.8	18
18:0	8	12	6	10	25	12.2	7
18:1	7	8	5	5	0	5	4
MEA	51	43	72	48	55	53.8	41
Others	26	26	9	20	trace	16.4	30

Data are expressed in percentages_and references are in brackets

1.11.7 Covalently Bound Internal Lipids of Animal Hairs

Korner and G. Wortmann [242] (Table 1.20), analyzed covalently bound fatty acids in isolated wool cuticle and found 55% 18-MEA, 25% stearic and 20% palmitic acid with "only traces of other straight and odd number carbon chain fatty acids." For wool fiber Wertz and Downing [259] found 48% 18-MEA and 17% palmitic acid, 10% stearic acid, 5% oleic acid and the remaining covalently bound fatty acids ranged from C16 through C20 with 6% uncharacterized. For human hair, Wertz and Downing [258] found 41% 18-MEA, 18%, palmitic acid, 7% stearic acid, 4% oleic acid and the remaining small percentages of fatty acids from C16 through C20 with 9% uncharacterized. Negri et al. [268] found 72% 18-MEA, 8% palmitic acid, 6% stearic acid and 5% oleic acid in wool fiber.

The variation in these data from different laboratories is quite large. Part of the variance must be related to fiber diameter and the number of layers of covalently bound fatty acids in the fibers. However, certainly part of this variance is due to experimental error. The bottom line is that somewhere in the vicinity of 50 $\pm$ about 10% of the covalently bound fatty acids in most keratin fibers is 18-MEA and that hair fibers from sheep, humans, dog, pig and cattle and likely most keratin fibers contain palmitic, stearic and oleic with other fatty acids as the remaining covalently bound fatty acids.

In 1990, Kalkbrenner et al. [269] demonstrated with isolated cuticle cells that 18-MEA is essentially all in the cuticle. Since 18-MEA represents more than 40% of the total covalently bound fatty acids in human hair and about 50% in wool fiber, 18-MEA is confined to the upper Beta layer of the cuticle [243, 244] while most (essentially an amount equal to the 18-MEA) of the other covalently bound fatty acids are confined to the lower Beta layer. Therefore, most of the covalently bound fatty acids in wool and hair fiber must be in the cuticle-cuticle CMC with some in the cuticle-cortex CMC (to be described later) and virtually none in the cortex-cortex CMC. Therefore, if most of the covalently bound fatty acids are in the cuticle-cuticle CMC, then most of the lipids of the cortex-cortex CMC must be bound to the membranes on one side and to the Delta layer on the other side by non-covalent bonds. The fact that most of the remaining lipids can be removed by solvent extraction confirms that this is the case.

Leeder et al. [128] were the first to report that there are virtually no phospholipids in keratin fibers. This fact was confirmed by Schwan and Zahn [270] and by Rivett [271] casting doubt on whether lipid bi-layers could be involved in the cell membranes of keratin fibers [128]. However, Wertz et al. [272] demonstrated that liposomes (lipid bi-layers and a presumed precursor to the formation of lipid bi-layers in the CMC of keratin fibers) can form from lipids in the absence of phospholipids if an acid species such as cholesterol sulfate is present. Furthermore, evidence has been provided confirming the existence of cholesterol sulfate in human hair by Wertz and Downing [258] and by Korner et al. in wool fiber [273].

The work of Korner, Petrovic and Hocker [273] builds upon the findings of Wertz et al. on liposome formation and lipids from stratum corneum [272]. Korner et al. [273] demonstrated that cell membrane lipids extracted from human hair and wool fiber with chloroform/methanol/aqueous potassium chloride can form liposomes. These findings provide evidence for a bi-layer structure of the internal lipids of the Beta layers of the cortical CMC in wool fiber and in human hair, see Fig. 1.45. Such extracts must come primarily from the cortex-cortex CMC because covalently bound MEA and the other covalently bound lipids of the cuticle CMC are not removed with this solvent system.

Therefore, if the Beta layers of the cuticle cells are primarily covalently bound fatty acids with some free lipids (see Fig. 1.44) and the Beta layers of cortical cells consist primarily of lipid bi-layers (Fig. 1.45), then it is highly probable that the proteins that these different types of lipid layers are attached to, that is the cell membrane proteins and the Delta layer proteins of the cuticle cells and the cortical cells, are also different.

1.11.8 Differences in Cuticle-Cuticle, Cortex-Cortex and Cuticle-Cortex CMC

As early as 1975, Nakamura et al. [233] provided evidence from staining reactions that the disulfide content in the Delta layer in cuticle-cuticle CMC is lower than the disulfide content of the Delta layer in either cuticle-cortex or cortex-cortex CMC. In addition, Nakamura et al. added that the Delta layer of the cuticle-cuticle CMC stains similar to the endocuticle.

In 1983, Leeder et al. [128] used TEM to study the effect of solvents on wool fibers and found that formic acid treatment of wool modified the CMC of the fibers. This effect was only observed between adjacent cortical cells and not between cuticle and cortical cells. These scientists suggested that these results are consistent with differences in the CMC between cuticle cells vs. the CMC between cuticle and cortical cells.

Peters and Bradbury [274] observed that formic acid treatment of wool modified the cell membrane complex of the cortex “but that of the cuticle appears unchanged”. They also analyzed “resistant membranes”. These membranes were isolated by shaking wool fibers in formic acid and then oxidized with performic acid. This treatment produced an oxidized cell membrane material; however, the amino acid analysis produced considerably lower values for cystine than the analysis of Allworden membranes by Allen et al. [132]. Peters and Bradbury concluded that the “CMC of the cuticle differs from that of the cortex”.

Leeder et al. in 1985 [275] described differences in the staining characteristics of the cuticle-cuticle CMC, the cuticle-cortex CMC and the cortex-cortex CMC. After dyeing the fibers with a Uranyl dye these scientists found a layer of dye around each cuticle cell that was restricted to the CMC of the cuticle and not in the CMC of the

cortex. They found only one dye layer at the cuticle-cortex junction and none in the cortex-cortex CMC, but two layers of dye in the cuticle-cuticle CMC. In their paper, these scientists referred to the observations of Nakamura [233] on differences in the staining characteristics of these three types of CMC.

Mansour and Jones in 1989 [261] treated wool by Soxhlet extraction with chloroform/methanol for 5 h and subsequently in boiling water for 15 min. They examined the fibers by electron microscopy after each stage of treatment. After the initial solvent extraction, the cuticle-cortex CMC appeared unmodified, while the staining intensity of the Beta layers between cortical cells were changed and appeared "intermittent". After solvent extraction for 5 h and hydrolysis for 15 min significant structural changes were observed. The cortex-cortex CMC showed an overall reduction in definition in the Delta layer and the Beta layers displayed a lack of clear definition. These scientists suggested that solvent extraction of intercellular lipids makes the hair more vulnerable to hydrolytic damage with the largest changes occurring in the cortex-cortex CMC. These scientists related this effect to a reduction in tear strength of wool fiber by solvent extraction and hydrolysis. These results show that the cuticle-cortex CMC behaves differently from the cortex-cortex CMC to solvent extraction. The cuticle-cortex CMC is damaged by solvent extraction and subsequent hydrolysis, but not as severely as the cortex-cortex CMC.

Logan, Jones and Rivett [262] in 1990 examined wool fibers by TEM after extraction with chloroform/methanol and found that the cuticle-cuticle CMC appeared unchanged compared to untreated fibers. On the other hand they found that the Delta layer in the cortex was smaller and displayed variable staining intensity in most regions which they deduced as "incomplete or preferential extraction". These scientists examined fiber sections after chloroform/methanol extraction followed by treatment with formic acid. They noted large changes in the Beta and Delta layers of the cortex-cortex CMC which were "rarely observed" in the cuticle-cuticle CMC. They concluded that these results show "inherent differences exist between CMC's of cuticle and those of cortical cells".

Negri and Rivett et al. [263] in a paper in 1996 referred to the work of Leeder et al. [275] and cited the work of Leeder et al. [128] who showed that the unstained Beta layers of the cuticle and cortex react differently to formic acid treatment. Leeder and Marshall [276] demonstrated that formic acid removes proteins from the cortex-cortex CMC and it modifies the CMC junctions of the cortex but not the cuticle-cuticle CMC junctions and they referenced Nakamura [233], and Leeder et al. [128] and Peters and Bradbury [274] on these effects. They concluded that these observations suggest that only the Beta layers of the cuticle-cuticle CMC contain covalently bound lipids while the Beta layers of the cortex contain lipids and a "stain-resistant membrane protein" that is "likely to be of a different structure than the cuticle membrane".

Inoue et al. in 2007 [277] analyzed human hair by microbeam x-ray diffraction after extraction with polar organic solvents (methanol or chloroform/methanol) at 37°C for 6 h. These treatments remove some material from the Delta layer of the cuticle-cuticle CMC, but the Beta layers were unaffected. On the other hand, the

Beta layers of the cuticle-cuticle CMC appeared to be affected by hexane extraction under the same conditions. The observation that changes in the Delta layer of the cuticle-cuticle CMC by chloroform/methanol extraction could be detected suggests this method is more sensitive than TEM [262]. The fact that Inoue et al. observed changes in the Beta layers of the cuticle-cuticle CMC by hexane extraction could result from removal of free lipids between the covalently bound fatty acids of the cuticle-cuticle CMC resulting in folding back of the covalently bound fatty acids in the Beta layers accounting for the differences found.

The above discussion shows clearly that both the lipid Beta layers and the proteins of the cell membranes and those of the Delta layer of the cuticle-cuticle CMC differ from those of the cortex-cortex CMC, with evidence for differences from the cuticle-cortex CMC also.

1.11.9 The Structure of the Cuticle-Cortex CMC

The following proposal for the cuticle-cortex CMC (Fig. 1.46) is based on logic and the following supporting evidence. The work of Nakamura [233] suggested that the cuticle-cortex CMC differs from both the cuticle-cuticle CMC and the cortex-cortex CMC. The work of Leeder et al. [128] and of Mansour and Jones [261] demonstrated that the cuticle-cortex CMC is more resistant to solvents than the cortex-cortex CMC. But, the most convincing evidence for this model (Fig. 1.46) is the Uranyl dye study by Leeder et al. [275]. Treatment of wool fiber with Uranyl dye showed two layers of dye in the cuticle-cuticle CMC, one layer of dye in the cuticle-cortex CMC and no layers of dye in the cortex-cortex CMC.

Since the cuticle-cortex CMC bridges cuticle and cortical cells, it is logical to assume that it is a hybrid based partly on the cuticle-cuticle CMC and the cortex-cortex CMC. Therefore, the membrane on the cuticle side would be the cuticle cell membrane which supports covalently bound fatty acids that are bonded either through thioester, ester or amide linkages and these covalently bound fatty acids are connected on their hydrophobic end to a hydrophobic protein in the Delta layer.

The membrane on the cortex side is a cortical cell membrane that supports fatty acids bound through polar and salt linkages as illustrated in the schematic of Fig. 1.46 and these fatty acids form a lipid bi-layer. The Delta layer of the cuticle-cortex CMC then should contain a hydrophobic protein on one side (bound to the Beta layer on the cuticle side) and a hydrophilic protein on the opposite side bound through polar and salt linkages to the lipid bi-layer. Leeder et al. [275] in their TEM study on dyeing and diffusion suggested that either the cuticle Beta layer or the resistant membrane surrounding cuticle cells has an affinity for the uranyl dye whereas the cortical cell membrane or the Delta layer between cortical cells does not. The models of Fig. 1.46 (for the cuticle-cortex CMC), Fig. 1.44 (for the cuticle-cuticle CMC) and Fig. 1.45 (for the cortex-cortex CMC) are consistent with the results and explanation by Leeder et al. [275] of the uranyl dye binding in the different CMC's.

1.11.10 The Formation of the CMC in Developing Hairs

The following description of the formation of the CMC in the developing hair fiber was taken from the work of Rogers [26], plus from the early work by Orwin and coworkers [278] along with more recent work by Jones and coworkers [279]. For more details of the formation of the CMC in developing hair fibers, I refer you to the review by Jones and Rivett [125] and this paper by Jones, Horr and Kaplin [279].

In the latter stages of development of the hair fiber, desmosomes or intercellular bridges, gap junctions (where cells exchange molecules) and tight junctions (intercellular junctions where cell membranes fuse) are established between differentiating keratinocytes of the hair fiber and the inner root sheath to varying extents as they move upward in the hair follicle. Orwin et al. [278] described that gap junctions and desmosomes cover about 10% of the plasma membrane of cortical cells in the bulb region and then they gradually degenerate.

Tight junctions are established between Henle's outermost layer of the inner root sheath and Huxley's layer of the inner root sheath and between Henle cells and the close companion layer of the outer root sheath. These junctions are replaced with a new cell membrane complex that gradually develops as a continuous complex between the cells. Similar events should occur for cuticle-cuticle CMC, cuticle-cortex CMC and cortex-cortex CMC with appropriate distinctions.

1.12 The Medulla

Fraser et al. [169] suggested that fine animal hairs such as merino wool—consist only of cuticle and cortex, but with increasing fiber thickness, a third type of cell, the medulla, is usually found (see Figs. 1.3, 1.4 and 1.48). In thick animal hairs such as horse tail or mane or porcupine quill, the medulla comprises a relatively large percentage of the fiber mass. However, in human hair, the medulla—if present—generally comprises only a small percentage of this mass. The medulla may be either completely absent, or highly variable [280], for example, it may be continuous along the fiber axis, or discontinuous. In some instances, a double or divided medulla may be observed (see Fig. 1.49).

Medullary cells are loosely packed, and during dehydration (formation), they leave a series of vacuoles along the fiber axis see Figs. 1.48 and 1.49. At higher magnification medullary cells appear spherical and hollow inside and are bound together by a cell membrane complex type material (see Fig. 1.50). Menkart et al. [156] suggested that the medulla contributes negligibly to the chemical and mechanical properties of human hair fibers. Therefore, for human hair, medulla is of greater importance to forensic science (for hair comparison identification) than to cosmetic science.

Das-Chaudhuri and Chopra [281] compared medulla with scalp hair fiber diameters for 12 different populations from different geographical regions. These

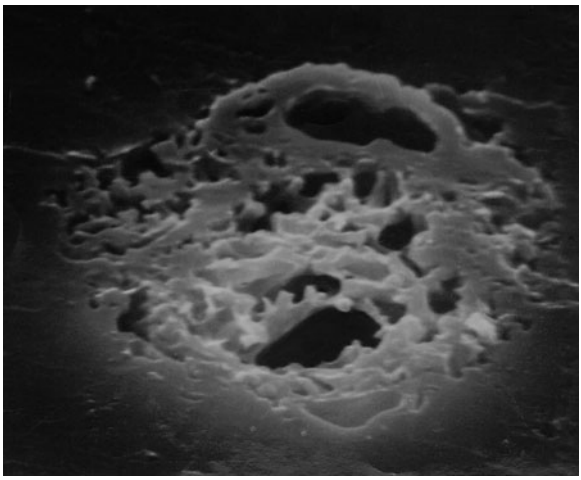

Fig. 1.48 Scanning electron micrograph illustrating the porous medulla of a hair fiber cross section

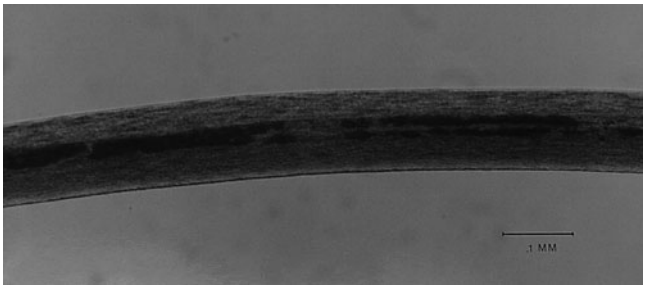

Fig. 1.49 An optical section of a light micrograph illustrating a hair fiber with a divided or double medulla. Multiple medullas seem more common in facial than scalp hair (Kindly provided by John T. Wilson)

scientists considered only hairs with and without medulla and considered a medullary ratio of P/Q where P represents the total number of medullated hairs and Q the number of total hairs. One hundred hairs per individual were examined. Their data provided a significant correlation between hair diameters and medulla with a correlation coefficient of 0.58 and an index of determination of 0.34.

Banerjee [282] collected data from 12 different populations in India where he considered hair fiber diameter and three medullation types: hairs with a continuous medulla, a discontinuous medulla and hairs with no medulla. Examination of the means of the different diameters of these three medulla classes by the matched pairs test shows a highly significant relationship with $p > t = 0.02$. The hairs with no medulla were the finest, those with a discontinuous medulla were medium in diameter and those with a continuous medulla were the coarsest. Hardy [106] also found a positive correlation between human scalp hair fiber diameter and medullation.

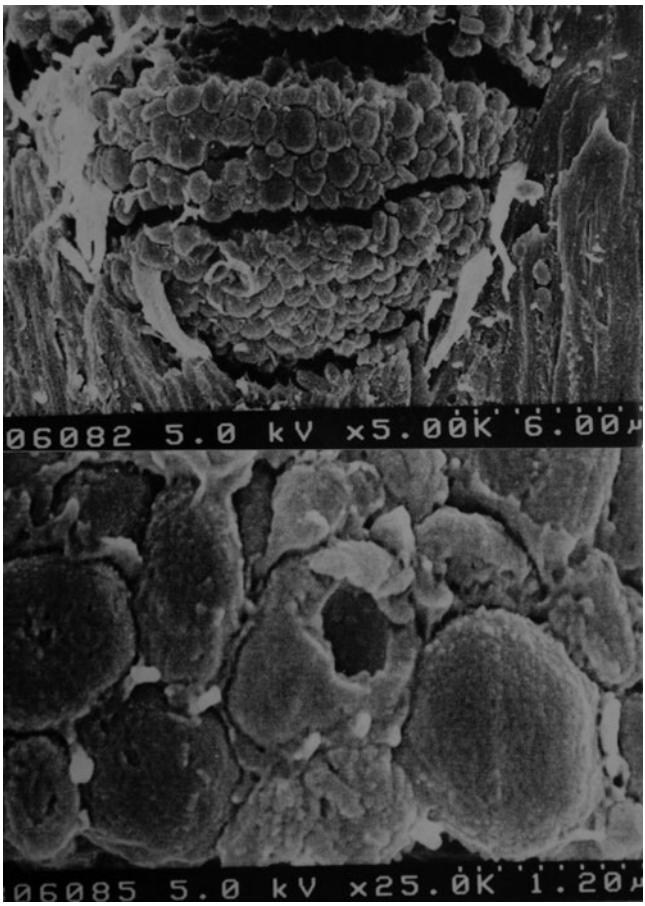

Fig. 1.50 Scanning electron micrograph illustrating the hollow sphere-like structures of the medulla (Kindly provided by Sigrid Ruetsch)

Wynkoop [283] classified hairs according to four different medulla types: absent, scanty, broken and continuous. She considered age and fiber diameter vs. medulla type. Wynkoop concluded that the amount and type of medulla are not related to age, but the amount of medulla is related to hair fiber diameter and that the finest hairs generally do not contain a medulla, medium-sized hairs generally contain a broken medulla and the thickest hairs generally contain a continuous medulla. So, there is a strong positive relationship between hair fiber diameter and the amount of medulla; thus fine hair of children generally does not contain a medulla [49], but coarser hairs of adults generally contains either a discontinuous or continuous medulla.

Tolgyesi [153] demonstrated that beard hair is coarser than scalp hair and it contains a higher percentage of medulla than scalp hair. There is generally more medulla in the coarser hairs of Asians than Caucasians; however, many Caucasian

hairs do contain medulla. The more fine the individual hair fiber, the lower the probability that medulla is present and the lower percentage of medulla mass.

At one time the presence of keratin proteins in the medulla was questioned [284]. In addition, Dobb [285] indicated that medulla of many hairs is difficult to isolate and therefore has received little scientific attention, however, Langbein et al. [280] demonstrated that several keratin proteins and a few cortical cells can be found in human beard hair medulla. These scientists found that 12 hair keratins and 12 epithelial keratins are potentially expressed in medullary cells and the keratin arrangement is very irregular in each medulla cell. The chemical composition of medullary protein derived from African porcupine quill has been reported by Rogers [205] and is described in Chap. 2 along with additional details on the composition of medulla from human beard hair and the medullary proteins by Langbein et al. [280].

The medulla does seem to play a role in gray hair, as suggested by Nagase et al. [286] by scattering light through a change in refractive index at the air to hair interface of medullary "pores". This effect is analogous to the effect in the genetic abnormality of pili annulati also known as ringed hair. Pili annulati appears as bands or rings of silver/gray and dark regions along the fiber axis. These bands are not associated with pigmentation. Musso [287] working with guidance from RDB Fraser observed that ringed hair contains bands or areas with air spaces in the cortex along the axis that correspond to the silver or gray bands. The air spaces are believed to be caused by a defect in the synthesis of the microfibril-matrix complex in the cortex, most likely with less being produced. This effect creates cavities or air spaces in the hair [287], see the section entitled *Hair Abnormalities* in Chap. 3. The medulla may also be involved in the splitting of hairs since in addition to the CMC it provides a pathway or an area of weakness for the propagation of cracks along the axis of the fiber as described by Kamath and Weigmann [200].

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Chapter 2
Chemical Composition of Different Hair Types

Abstract Human hair consists of proteins, lipids, water, trace elements and pigments. The composition of the first four of these components is the focus of this Chapter. About two decades ago the emphasis on the proteins of hair was on its amino acid constituents which provided important information on the relative amounts of different functional groups in different types of hair and in different regions of the fiber. However, as a result of advances in the characterization and classification of the different proteins and genes of keratins and keratin associated proteins the focus today is on the proteins themselves. Several important new contributions to the composition of the surface layers of hair and the proteins of the cell membrane complex have been and are continuing and therefore are summarized in this Chapter. The current state of changes in the amino acids, proteins and lipids of hair by morphological region (including KAP and keratin proteins and where they reside), chemical and sunlight damage, diet, puberty and menopause, and other factors have been and are being made and are summarized here. An expanded section on metals in hair, where in the fiber these metals reside and the functional groups that they bind to and their effects on hair chemistry, toxicity and disorders are included.

2.1 Introduction

Several important new and relatively recent contributions to the structure of the cell membrane complex, the composition of the surface layers of hair, the overall structure of the hair fiber and its follicle have been added to this Chapter. Recent studies revealed details about endogenous and exogenous hair lipids and the critical involvement of proteins and free lipids in the surface layers of hair including lipid contributions to the protective properties of the cuticle and the isoelectric point. Advances in the classification and characterization of the different proteins and genes involved in keratin and keratin associated proteins in human hair are summarized in this Chapter and the analysis of protein fragments from hair

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damaged by cosmetic chemicals is a new and exciting area for future research. The effects of menopause on changes in the lipids of scalp hair have been added to this Chapter and the recently found effects of menopause on the diameter of hair fibers have been added to Chap. 9.

Human hair is a complex tissue consisting of several morphological components (see Chap. 1), and each component consists of several different chemical types [1]. Hair is an integrated system in terms of its structure and its chemical and physical behavior wherein its components can act separately or as a unit. For example, the frictional behavior of hair is related primarily to the cuticle, yet, the cuticle, the cortex and its intercellular components act in concert to determine the softness of hair. The tensile behavior of human hair is determined largely by the cortex, yet we have learned that the physical integrity of the fiber to combing and grooming forces is also affected by the non-keratin components of the cuticle and the cell membrane complex. Nevertheless, for simplicity and ease of discussion, the different types of chemicals that comprise human hair are generally described separately in this Chapter.

Depending on its moisture content (up to 32% by weight), human hair, consists of approximately 65% to 95% proteins. Proteins are condensation polymers of amino acids. The structures of those amino acids that are found in human hair are depicted in Table 2.1. Because of the large number of chemical reactions that human hair is subjected to by permanent waves, chemical bleaches, alkaline straighteners and sunlight exposure, many of the proteins are fragmented and several of these amino acids are converted to amino acid derivatives depicted in Table 2.2. The remaining constituents are water, lipids (structural and free), pigment, and trace elements that are generally not free, but combined chemically with side chains of protein groups or with fatty-acid groups of sorbed or bound lipid. These different components of hair: proteins, lipids, water and trace elements are described separately in this Chapter while pigments are described in more detail in Chap. 5.

Studies of the proteinaceous matter of human hair may be classified according to the following types of investigation:

Studies of individual or several amino acids,
Analysis of types of amino acids,
Fractionation and peptide analysis,
Expression of genes, using in situ hybridization or reverse transcriptase-polymerase chain reaction (RT-PCR) expression by hair follicles or the use of specific protein antibodies or related techniques.

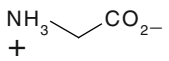
Most studies of individual amino acids of keratin fibers involve the amino acids cystine or tryptophan. Quantitation of cystine can be accomplished by chemical analysis of mercaptan with [2, 3] or without hydrolysis [4] or spectrophotometrically on intact hair [5, 6]. With increasing sophistication in instrumental analysis, ESCA, SIMS, and different absorbance, reflectance and fluorescence techniques, spectrophotometric analysis on intact hair is becoming increasingly important.

Chemical analyses for tryptophan have been described by Block and Bolling [7] and are all hydrolytic procedures.

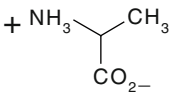
McMillen and Jachowicz [8] based on prior work in the wool industry analyzed tryptophan and its kynurenine reaction products by fluorescence spectroscopy using excitation wavelengths of 290, 320 and 350 nm which provides emission bands at 345, 420 and 465 nm. The emission band with a maximum at 345 nm corresponds to Tryptophan with an absorption maximum at about 360 nm. The emission peak at 465 nm from excitation at 320 and 350 nm matches the emission band of 1-kynurenine which has an absorption maximum at about 360 nm. The emission maximum at 420 nm was ascribed to N-Formylkynurenine and has an absorption

Table 2.1 Structures of amino acids found in hydrolyzates from human hair (molecular weights of these amino acids are listed in brackets)

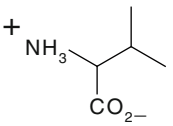
Aliphatic Hydrocarbon R Group



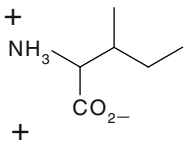
Glycine [75]



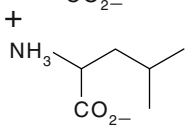
Alanine [89]



Valine [117]

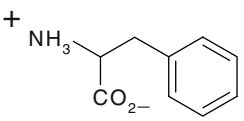


Isoleucine [131]

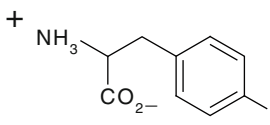


Leucine [131]

Aromatic Hydrocarbon R group

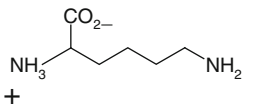


Phenylalanine [165]

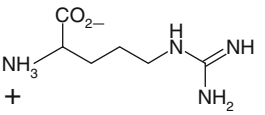


Tyrosine [181]

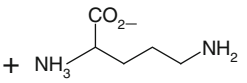
Diacidic Amino Acids



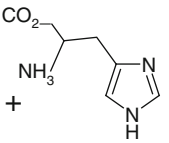
Lysine [146]



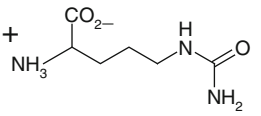
Arginine [174]



Ornithine [132]

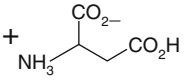


Histidine [155]

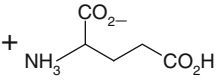


Citrulline [175]

Diacidic Amino Acids

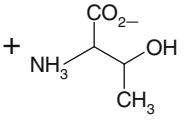


Aspartic Acid [133]

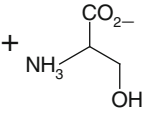


Glutamic Acid [147]

Hydroxyl containing amino acids

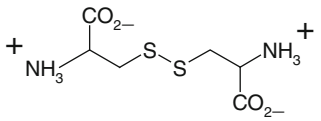


Threonine [119]

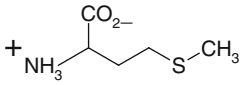


Serine [105]

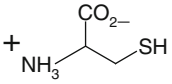
Sulfur containing amino acids



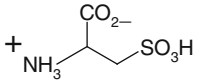
Cystine [240]



Methionine [149]

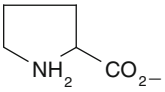


Cysteine [121]

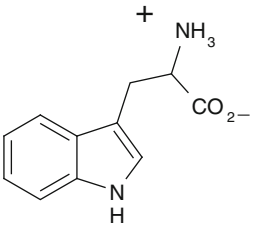


Cysteic Acid [169]

Heterocyclic amino acids in hair



Proline [115]



Tryptophan [204]

Aspartic acid and glutamic acids exist as the primary amides and the free acids in human hair

maximum at 320 nm. In this paper on thermal degradation of hair, the authors claimed that the spectra after thermal exposure indicate a decrease in the emission intensities of all bands, probably related to thermal decomposition of the corresponding chromophores. The largest reduction in the emission intensity is evident for the band at 345 nm corresponding to Tryptophan providing evidence for its photochemical degradation.

Quantitative determination of several amino acids in human hair became increasingly widespread years ago following the development of the ion exchange chromatographic systems of Moore and Stein [9]. But more recently, protein

Table 2.2 Structure of amino acid degradation/derivative products found in human hair[a]

Derivatives of cystine
Cystine oxidation products from peroxide bleaching
–CH–CH_2–S–SO–CH_2–CH– cystine monoxide
–CH–CH_2–S–SO_2–CH_2–CH– cystine dioxide
–CH–CH_2–SO_3M cysteic acid salt
From sulfite perms and sunlight oxidation
–CH–CH_2–S–SO_3M Bunte salt
From TGA perms
–CH–CH_2–S–S–CH_2–CO_2M
From GMT perms
–CH–CH_2–S–S–CH_2–CO–O–CH_2–CH(OH)–CH_2–OH
Hydrolysis gives the derivative above from TGA perms
From cysteamine perms
–CH–CH2–S–S–CH_2–CH_2–NH_2*HX
From strong alkalinity as (straighteners, perms, bleaches)
–CH–CH_2–S–CH_2–CH– lanthionine
–CH–CH_2–NH–$(CH_2)_4$–CH– lysinoalanine
Derivatives of amino acids other than cystine
From strong alkalies (hydrolysis of amides)
–CH–CH_2–CO_2M
–CH–CH_2–CH_2–CO_2M
From chemical oxidation
–CH–CH_2–CH_2–SO_2–CH_3 methionine sulfone (sulfoxide not demonstrated)
From TGA perms
–CH–$(CH_2)_4$–NH–CO–CH_2–SH thioacetylated lysine
From sunlight oxidation
–CO–CO–R alpha keto derivatives and cross-links of these with amino groups

[a]Degradation of other amino acids such as tryptophan, lysine and histidine are known to occur from sun exposure, however, identification of the degradation products has not been made

sequencing techniques such as the use of Polymerase chain reaction (PCR) primers, or analysis of cDNA's with sequences that code specific proteins or even digestion to specific peptides and analysis by mass spectrometry or the use of specific protein antibodies or other techniques have become increasingly important. Studies of amino acid types are also used today, but less frequently. These involve determination of a specific functional group where more than one amino acid contains that type of group such as, the titration of basic groups [10] and of acidic groups [10].

Fractionation and peptide analysis is concerned primarily with fractionation into similar peptide types or even fractionation into the different morphological components. Major areas of hair research concerned with the chemical composition of hair and wool fibers, over the last two decades, have involved proteomics or the determination of the total proteins present in a fraction or region of the hair. This definition has been extended by some to include determining the proteins from

which fractions are derived from chemical degradation of hair by perming, oxidation and straightening reactions. Several important papers have been published defining and classifying the types of proteins in human hair fibers. An initial classification of hair proteins was described by Powell and G.E. Rogers. Important additions to this work have been reviewed in papers by M.A. Rogers and Langbein et al. that are described in detail and referenced in Chap. 1 as well as in this Chapter in the section entitled, *Major Protein Fractions of Hair*. In addition, the structure, composition and degradation of the cuticle, the cortex and medulla, the cell membrane complex and the composition of structural hair lipids are the major focus of this Chapter.

2.2 The Amino Acids and Proteins of Different Types of Hair

2.2.1 Whole-Fiber Amino Acid Studies

More than three decades ago, a large number of investigations were described on the analysis of the amino acids of whole human hair fibers. Whole-fiber amino acid analysis has several limitations, because it provides average values for the amino acid contents of the average proteinaceous substances of the fibers. Therefore, for whole-fiber results, cross-sectional and axial differences in the composition of the fibers are averaged.

A second complicating factor is hydrolytic decomposition of certain amino acids. The most commonly used medium for keratin fiber hydrolysis is 5–6 N hydrochloric acid. In studies involving acid hydrolysis of keratins, partial decomposition has been reported for cystine, threonine, tyrosine [11], phenylalanine, and arginine [12] with virtually complete destruction of tryptophan [12].

With the above limitations in mind, the following discussion describes several important factors contributing to differences in the whole-fiber amino acid analysis results of human hair, reported in the literature.

2.2.1.1 Unaltered or “Virgin” Human Hair

Unaltered human hair is hair that has not been chemically modified by treatment with bleaches, permanent waves, straighteners, or hair dyes. Numerous publications [7, 13–28] describe results of the amino acid analysis of unaltered human hair. Table 2.1 depicts the structures for 22 amino acids that have been identified in human hair. Cysteic acid and other amino acids, derived from those amino acids of Table 2.1, are also present in either weathered or cosmetically altered hair, see Table 2.2. Table 2.3 summarizes results from several sources describing quantitative whole fiber analyses of these 22 amino acids. These same amino acids are classified according to functional group in Table 2.4.

Table 2.3 Amino acids in whole unaltered[a] human hair (micromoles per gram dry hair)

Amino acid	Reference [13]	Reference [14]	Other references
1. Aspartic acid	444–453[b]	292–578[c]	
2. Threonine	648–673[b]	588–714	
3. Serine	1,013–1091[b]	705–1,090	
4. Glutamic acid	995–1036[b]	930–970	
5. Proline	646–708[d]	374–694[d]	
6. Glycine	463–513[d]	548–560	
7. Alanine	362–384[d]	314	
8. Half-cystine	1,407–1,512[d]	1,380–1,500	784–1,534 [15][d]
9. Valine	477–513[d]	470	
10. Methionine	50–56[b]	47–67	
11. Isoleucine	244–255[d]	366	
12. Leucine	502–529[d]	489[c]	
13. Tyrosine	177–195[d]	121–171[c]	
14. Phenylalanine	132–149[d]	151–226	
15. Cysteic acid	22–40[d]	–	
16. Lysine	206–222[b]	130–212[c]	
17. Histidine	64–86[d]	40–77	
18. Arginine	499–550[d]	511–620	
19. Cysteine	–	41–66	17–70 [15][d]
20. Tryptophan	–	20–64	
21. Citrulline	–	–	11 [17]
% Nitrogen as ammonia		15.5–16.9%	16.5% [16]

[a]Hair is assumed to be cosmetically unaltered for Refs. [14, 15, 17]
[b]No significant differences among samples analyzed
[c]The circled values are results of a microbiological assay by Lang and Lucas [18]
[d]Significant differences indicated among samples analyzed
[e]These results are a compilation of results from several laboratories and therefore contain no basis for statistical comparison of each individual amino acid from the different laboratories

Note the high frequencies of hydrocarbon, hydroxyl, primary amide, and basic amino acid functions in addition to the relatively large disulfide content. The high frequency of hydrocarbon-containing amino acids confirms that hydrophobic interactions play a strong role in the reactivity of hair toward cosmetic ingredients. Hydroxyl and amide groups interact through hydrogen bonding interactions, while the basic and carboxylic acid groups interact through hydrogen bonding and ionic bonding type interactions.

Of particular note is the fact that most of these functional groups occur at higher frequencies than the disulfide bond in hair. However, these frequencies are whole-fiber frequencies, therein assuming that hair is a homogeneous substrate. This assumption is certainly not the case, as subsequent sections of this Chapter demonstrate.

Table 2.3 shows substantial variation in the quantities of some of the amino acids, notably aspartic acid, proline, cystine, and serine, while considerably less

Table 2.4 Approximate composition unaltered human hair by amino acid side-chain type

Amino acid side-chain type[a]	Approximate micromoles per gram hair
1. *Hydrocarbon* (except phenylalanine)	2,800
Glycine, alanine, valine, leucine, isoleucine, and proline	
2. *Hydroxyl*	1,750
Serine and threonine	
3. *Primary amide + carboxylic acid*	1,450
Primary amide (ammonia estimation)	1,125
Carboxylic acid (by difference)	325
4. *Basic amino acids*	800
Arginine, lysine, and histidine	
5. *Disulfide*	750
Cystine	
6. *Phenolic*	180
Tyrosine	

[a]See Table 2.3

dispersion is indicated for valine, glutamic acid, glycine, alanine, leucine, and arginine.

The following factors can produce differences in whole-fiber amino acid analysis results; genetics, weathering (primarily sunlight exposure), cosmetic treatment, experimental procedures, and diet (not normal diets of healthy individuals, but protein deficient diets).

Marshall and Gillespie [29] proposed special mathematical relationships between cystine and leucine:

- Leucine (residue %) = −0.31 × half-cystine (residue %) + 11.3 and between cystine and proline to determine abnormal variations:
- Proline (residue %) = 0.26 × half-cystine (residue %) + 3.8

These relationships are based on the fact that leucine and cystine are common components of the low sulfur proteins, while proline and cystine are primary components of the high sulfur proteins. They further suggest that the cystine content should be about 17–18% and that large variations beyond the calculated values for these three amino acids indicates some cause of variation such as genetic, environmental (sunlight exposure), cosmetic treatment, diet, etc. Variation from these factors is described next.

2.2.1.2 Amino Acid Composition Related to Genetics

The variation of cystine and cysteine in human hair has been studied extensively. Clay et al. [15] quantitatively analyzed hair from 120 different persons for cystine and cysteine (see Table 2.3). The hair in this study was selected from both males and females of varying age and pigmentation. Analysis was by the hydrolytic

method of Shinohara [30]. These results show a wide spread in disulfide content varying from 784 to 1,534 μmol half-cystine per gram of hair (8.7–17%); substantially different from the cystine level suggested by Marshall and Gillespie for "normal" hair. Significantly more cystine was found in hair from males than females. Also, dark hair generally contained more cystine than light hair. A similar relationship between cystine content and hair color has been reported by Ogura et al. [31].

No consistent relationship was found between age and cystine content. Although factors such as diet (malnutrition), cosmetic treatment, and environmental effects (sunlight degradation) may have contributed to variation among these samples, such factors were not considered in this study.

With regard to racial variation, nothing has been definitely established. Hawk's data [23] appears to show subtle differences in the relative percentages of various amino acids found in the hydrolysates of African hair compared to Caucasian hair. Wolfram compiled a more complete set of data from the literature of whole-fiber amino acid analysis of the three major geo-racial groups, showing overlap in the amounts of all the amino acids from scalp hair for these three groups [32]. See the section in Chap. 1 entitled *The Origin of Hair Fiber Curvature* which explains the distribution and composition of different types of cortical cells in hair. Quantitative protein techniques in the section entitled *Major Protein Fractions of Hair* in this Chapter and SNP analysis (Chap. 3) rather than amino acid analysis provides the best means for determining the differences in the proteins of scalp hair of different geo-racial groups.

2.2.1.3 Weathering of Human Hair

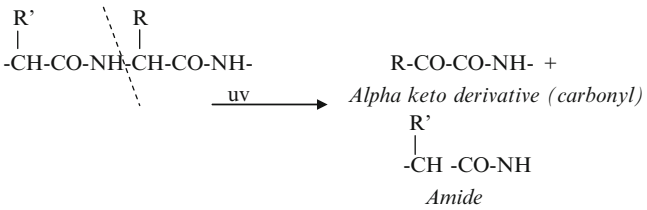
The photochemical degradation of cystine (see Chap. 5) provides a major cause for variation in this amino acid among different hair samples. Weathering effects [33] in human hair may be explored by comparing tip ends (longer exposed) to root ends. In a study by Robbins, the cystine and cysteine contents of tip ends were shown to be lower than in root ends [34]. Complementary to these results, larger amounts of cysteic acid have been reported in hydrolysates of tip ends of human hair than in root ends [13]. Evidence for cysteic acid in weathered wool has also been provided by Strasheim and Buijs by infrared spectroscopy [35] and for some South African Merino wools by Louw [36].

These results suggest conversion of thioester and cystinyl groups in human hair to higher oxidation states by the elements. This conclusion is supported by the work of Harris and Smith [37], who determined that ultraviolet light disrupts the disulfide bond of dry wool. In another study, Robbins and Bahl [6] examined both the effects of ultraviolet light on hair from root and tip sections from several persons using electron spectroscopy for chemical analysis (ESCA) to examine different types of sulfur in hair. Their data suggested that weathering of cystine in hair is primarily a

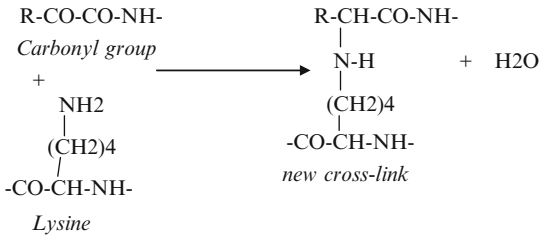
photochemical reaction proceeding mainly through the C-S fission route producing cystine S-sulfonate residues as a primary end product. This reaction also occurs to a greater extent near the fiber surface showing that oxidation of thioester to sulfonate and loss of MEA also occurs by photochemical degradation. McMillen and Jachowicz [8] found that Tryptophan is sensitive to degradation by heat. It is also sensitive to photochemical degradation. Significantly lower quantities of the dibasic amino acids lysine and histidine have been reported in tip ends of human hair compared to root ends [34].

As indicated, for hair damaged by sunlight, in most cases, the amino acids of the cuticle are altered to a greater extent than those of the cortex because the outer layers of the fiber receive higher intensities of radiation. Hair protein degradation by light radiation has been shown to occur primarily in the wavelength region of 254–400 nm. More recent work by Hoting and Zimmerman [38] shows that the proteins of the cuticle are degraded by UV-B and UV-A, but less by visible light and that cystine, proline and valine are degraded more in light brown hair than in black hair. In other words the photo-protective effect of melanin is much better in dark hair than in light hair.

Oxidation at the peptide backbone carbon has been shown to occur from ultraviolet exposure both in wool [39] and in hair [6, 40], producing carbonyl (alpha keto amide intermediates as shown below) which are favored in the dry state reaction more than in the wet state. This reaction is similar to the oxidative damage to proteins and mitochondrial decay associated with aging described by Dean et al. [41] and described in detail in Chap. 5.



The photochemical breakdown of disulfide bridges within structural units of the A-layer and the exocuticle and matrix of the cortex and the establishment of new intra- and intermolecular cross-links via reaction of these carbonyl groups (from uv degradation) with protein amino groups (primarily lysine as shown below) within and between structural units decreases structural definition. These reactions most likely lead to a gradual increase in brittleness and a gradual loss of structural differentiation, see Chap. 5 for details and micrographs that support these conclusions.



2.2.1.4 Experimental Procedures

The inconsistent use of correction factors to compensate for hydrolytic decomposition of certain of the amino acids has already been described. In addition, methods of analysis described in the literature have ranged from wet chemical [20], to chromatographic [13], to microbiological [18]. Reexamination of Table 2.3 with this latter condition in mind shows values for aspartic acid, proline, tyrosine, and lysine as determined by the microbiological assay to be in relatively poor agreement with the other values for these same amino acids determined by wet chemical and chromatographic procedures. In the case of valine, the values for the microbiological and chromatographic procedures are in close agreement. This suggests that for certain of the amino acids (valine) the microbiological assay is satisfactory, whereas for other amino acids (aspartic acid, proline, tyrosine, and lysine), the microbiological method is questionable.

2.2.1.5 Stability of Hair Keratin

Several years ago, a well-preserved cadaver was discovered by archaeologists in the Han Tomb No. 1 near Changsha, China [42]. In the casket, the occupant wore a well preserved hair piece that was more than 2,000 years old. Although this hair was not analyzed for amino acid content, it was analyzed by x-ray diffraction by Kenney [42], revealing that the alpha-helical content had been well preserved. Nevertheless, some minor disruption of the low ordered matrix had occurred owing to reaction with a mercurial preservative in the casket. This suggests that the basic structure of the intermediate filaments of human hair remains unchanged over centuries and its essential structural features are extraordinarily stable but the mercury preservative may be reacting with cystine in the matrix.

2.2.1.6 Cosmetically Altered Hair

Bleached Hair

The whole-fiber amino acid composition of human hair, bleached on the head with commercial hair-bleaching agents – alkaline hydrogen peroxide or alkaline

peroxide/persulfate [43] has been described in the literature [11]. This investigation defines the amino acids found in hydrolysates of hair bleached to varying extents on the head. Data describing frosted (extensively bleached hair using alkaline peroxide/persulfate) vs. non-bleached hair from the same person, bleached on the head about 1 month prior to sampling, are summarized in Table 2.5. These data show that the primary chemical differences between extensively bleached hair and unaltered hair are lower cystine content, a higher cysteic acid content, and lower amounts of tyrosine and methionine in the bleached hair. Mildly to moderately bleached hair shows only significantly lower cystine and correspondingly more cysteic acid than unaltered hair. These results support Zahn's [44] original conclusion that the reaction of bleaching agents with human hair protein occurs primarily at the disulfide bonds. Fewer total micromoles of amino acids per gram of hair are found in bleached than in unaltered hair (see Table 2.5) most likely because of addition of oxygen to the sulfur containing amino acids and to solubilization of protein or protein derived species into the bleach bath [45].

Products of disulfide oxidation, intermediate in oxidation state between cystine and cysteic acid (see Table 2.6), have been shown to be present in wool oxidized by aqueous peracetic acid [46–48]. These same cystine oxides have been demonstrated at low levels in bleached hair [49]; however, disulfide oxidation intermediates have not been shown to exist in more than trace amounts in hair oxidized by currently used bleaching products [50].

The actual presence of large amounts of cysteic acid in bleached hair had at one time been in doubt [51, 52]. It had been theorized that the cysteic acid found in

Table 2.5 Amino acids from frosted vs. non-frosted hair

Amino acid	Micromoles per gram hair		Significant difference for frequencies at alpha = 0.01 level
	Non-frosted fibers	Frosted fibers	
Aspartic acid	437	432	–
Threonine	616	588	–
Serine	1,085	973	–
Glutamic acid	1,030	999	–
Proline	639	582	–
Glycine	450	415	–
Alanine	370	357	–
Half cystine	1,509	731	Yes
Valine	487	464	–
Methionine	50	38	Yes
Isoleucine	227	220	–
Leucine	509	485	–
Tyrosine	183	146	Yes
Phenylalanine	139	129	–
Cysteic acid	27	655	Yes
Lysine	198	180	–
Histidine	65	55	–
Arginine	511	486	–

Table 2.6 Some possible oxidation products of the disulfide bond

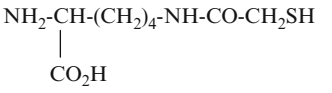
Formula	Name
R–SO–S–R	Disulfide monoxide
$R–SO_2–S–R$	Disulfide dioxide
$R–SO_2–SOR$	Disulfide trioxide
$R–SO_2–SO_2–R$	Disulfide tetroxide
$R–S–SO_3H$	Bunte acid or thiosulfonic acid
$R–SO_3H$	Sulfonic acid

bleached hair hydrolysates was formed by decomposition of intermediate oxidation products of cystine during hydrolysis prior to the analytical procedure [51]. However, differential infrared spectroscopy [5] and electron spectroscopy for chemical analysis by Robbins and Bahl [6] on intact un-hydrolyzed hair have conclusively demonstrated the existence of relatively large quantities of cysteic acid residues in chemically bleached hair. Evidence for other sulfur acids, e.g., sulfinic or sulfenic acids, in bleached hair has not been provided. Furthermore, it is unlikely that these amino acids exist in high concentrations in hair, because they are relatively unstable. For details concerning the mechanism of oxidation of sulfur in hair, see Chap. 5.

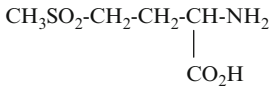
Permanent-Waved Hair

Nineteen amino acids in human hair have been studied for possible modification during permanent waving, that is all of the amino acids of Table 2.1 except tryptophan, citrulline and ornithine. Significant decreases in cystine (2–14%) and corresponding increases in cysteic acid [2, 11] and in cysteine [2] have been reported for human hair that has been treated either on the head by home permanent-waving products or in the laboratory by thioglycolic acid and hydrogen peroxide, in a simulated permanent-waving process.

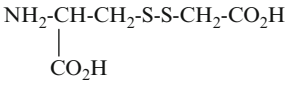
Trace quantities (less than 10 μmol/g) of thioacetylated lysine and sorbed thioglycolic acid have also been reported in human hair treated by cold-waving reagents [2]. Small quantities of mixed disulfide [2, 6], sorbed dithiodiglycolic acid [2], and methionine sulfone [11] have been found in hydrolyzates of hair treated by the thioglycolate cold-waving process.



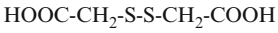
Thioacetylated lysine



Methionine sulfone



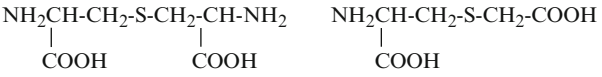
Mixed disulfide



Dithiodiglycolic acid

Methionine sulfone is presumably formed by reaction of the neutralizer with methionine residues; thioacetylated lyine is probably formed by reaction of lysine with thioglycolide impurity in the thioglycolic acid [2]. The mixed disulfide is presumably formed by displacement of thioglycolate on the cystine residues in hair (see Chap. 4 for mechanistic details). One might also expect to find trace quantities of methionine sulfoxide in hair; however, to date this sulfoxide has not been reported.

In alkaline media, the formation of lanthionine residues can also occur [53], see Chap. 4. Zahn et al. [54, 55] reported that thioglycolate can accelerate the rate of formation of thioether residues (lanthionyl) in wool fiber. Therefore, one might expect to find trace quantities of this amino acid in hair permanent-waved in an alkaline medium. Chao et al. [56] demonstrated small quantities of lanthionine and carboxymethyl thiocysteine (see Chap. 4) in hair reduced by thioglycolic acid.



Lanthionine

Carboxymethyl thiocysteine (mixed disulfide above)

Analytical procedures involving reduction and determination of mercaptan are not accurate determinations of cystine in permanent-waved hair or in hair treated with mercaptan, because mixed disulfide is reduced to mercaptan during analysis, and adsorbed mercaptan can also interfere in the determination. Procedures that do not involve reduction of hair such as ninhydrin detection (alpha-amino group) or dinitrofluorobenzene (DNFB) reaction followed by chromatographic separation [1, 54] discriminate between mercaptans and therefore should be better analytical procedures for detecting the different types of mercaptans and disulfides actually present in permanent waved hair.

Hair Straightened with Alkaline Straighteners

The process of straightening hair with alkaline straighteners is described in Chap. 4 and as shown in that section, relatively large quantities of lanthionine (>100 μmol/g) can be found in hair treated with these products that vary from pH 12 to above 13. Relatively large quantities of residues of the diacidic amino acids of aspartic and glutamic acids resulting from the alkaline hydrolysis of the corresponding amide residues would also be expected.

2.2.1.7 Analysis of Acidic and Basic Groups in Whole Human Hair

Both the acid-combining capacity [57, 58] and the acid dye-combining capacity [34, 59] of unaltered keratin fibers have been used to estimate the frequency of basic groups. Similarly, the base-combining capacity can be used to estimate the frequency of acidic groups in hair [57]. The acid-combining capacity of unaltered

human hair fibers is approximately 820 μmol/g [34, 59, 60]. This parameter provides an estimate of the frequency of basic amino acid residues, including N-terminal groups (approximately 15 μmol/g) [10, 61] and sorbed alkaline matter, whereas the base-combining capacity provides an estimation of the titratable acidic groups in the fibers, including C-terminal amino acid residues and any sorbed acidic matter.

Alterations to the fibers that affect the apparent frequency of acidic or basic groups, such as hydrolysis, susceptibility to hydrolysis, or the introduction of sulfonic acid groups [25], can affect the acid- and/or base-combining capacity of hair. Therefore, permanent-waving and especially bleaching (oxidation) can affect these titration parameters [11]. The effects of cosmetic treatments and environment on these titration parameters are described in detail in Chap. 6.

2.3 Aging Influences on Hair

As a person ages, hormonal changes contribute to changes in the hair. The more obvious changes are: Hair thickness (hair density or hairs/cm^2), hair graying (see Chap. 7), hair diameter (fine-coarseness) and dryness of the scalp and the hair. Hair thinning tends to relate to hair density and therefore to not to be noticeable in women until the mid to late twenties or more commonly a few years later, see Chap. 1 in *Hair Density versus Age for Caucasian Women*. Large increases in hair fiber diameter occur during the first year in life and during the teenage years. Diameter tends to peak at about age 20 for men and in the mid-forties for women, see Fig. 2.1. Figure 2.1 shows a steeper drop for the scalp hair fiber diameter of Japanese males vs. Caucasian males. This effect should be reexamined. Then, with increasing age hair fiber diameter decreases, see Chap. 9 in the section entitled *Fiber Diameter, Cross-sectional Area, Fine-coarse Hair and Age and Hair Growth* and references [62–65].

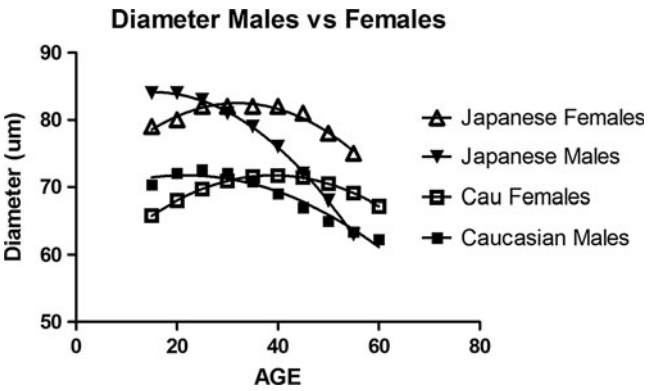


Fig. 2.1 The variation of hair fiber diameter with age and sex

Graying of hair relates to the size and distribution of the melanin granules as well as the types of pigments in the fibers. Gray hair is also dependent on the production of less pigment in the individual hairs with advancing age. It is usually associated with middle age; however, graying can begin in one's early 20s. For more details on the incidence of graying and the age that graying begins, see Chap. 7 in *Gray Hair and Graying of Human Hair*. The formation of hair pigments takes place in the melanocytes in the bulb of the follicle starting with the amino acid tyrosine as described in Chap. 5 in *Hair Pigment Structure and Chemical Oxidation*. Graying occurs when the melanocytes become less active during anagen. The melanin pigments are incorporated into large granules that are transferred into the keratin cells in the zone of keratinization, see Chap. 1.

Hollfelder et al. [66] provided some evidence (from hair from only five individuals) that gray hairs are coarser and wavier than heavily pigmented hairs on the same person. Van Neste [67] found that white hairs are coarser than pigmented hairs and that white hairs have more medulla. However, Gao and Bedell [68] studied gray and dark hairs from only four persons plus one sample of pooled gray hair. They found no significant differences in the maximum center diameter, center ellipticity and cross-sectional areas of gray vs. dark hairs. See Chap. 5 in the section entitled *Hair Pigment Structure and Chemical Oxidation* for additional details.

Less pigmented hairs, such as gray hairs [68], blonde hair or bleached hairs are also more sensitive to light radiation than heavily pigmented hairs. Therefore, lightly pigmented hairs exposed to ultraviolet radiation for a sufficient period will show lower levels of cystine and correspondingly higher levels of cysteic acid particularly in their outer layers when compared to heavily pigmented hairs. In addition damage to the cell membrane complex and tryptophan and other amino acids should occur at a faster rate in gray hair vs. heavily pigmented hairs. Such exposed gray fibers will also provide lower tensile stresses to achieve a given strain level in load-elongation tests and lower bending stiffness see Chap. 5 in *Hair Pigment Structure and Chemical Oxidation*.

Dryness/oiliness is another hair property associated with aging. There are two primary sources of hair lipids: The sebaceous glands and the hair matrix cells. Sebaceous glands occur over most of the body where hair fibers exist. These glands excrete their oils through the narrow opening of the hair follicle onto hair and skin surfaces. The output of these glands is related to the size of the gland, age and sex. Prior to puberty, the output of these glands is low and the hair tends to be dry, see the section entitled, *Free Lipids in the Total Hair Fiber* in this Chapter. Sebaceous output increases at puberty through the teenage years and into the second decade. With increasing age beyond the fourth decade, sebum output decreases, but more so in females than in males.

Changes in the composition and amounts of hair lipids on and in the fibers, lower scalp hair density, lower growth rates and lower hair fiber diameters occur with advancing age. These changes affect important hair properties beyond the mid-forties especially for women because these effects are exacerbated by menopause

when hair lipid changes have been shown to make hair on the head less greasy or drier, see *The effects of Menopause on the Lipids in Hair and on the Hair Fiber,* described later in this Chapter. A decrease in softness and smoothness of the hair of post-menopausal women has also been reported.

It is also likely that hair curvature increases with advancing age as has been shown for Japanese women see Chap. 10 in the section entitled *Hair Handle or Feel*. This effect will likely make the hair fibers more prone to frizziness and will decrease hair luster as shown for Japanese hair.

The effects of these age related changes in hair density, diameter or area of cross-section, graying, curvature and hair lipids produce changes in fiber properties which produce changes in important consumer hair assembly properties such as a changes in combing ease, hair body, hair coverage, frizziness, manageability, style retention, etc. which are described in detail in the last section of Chap. 10.

Aging of individual hair fibers on one's head by everyday grooming actions generally results in a gradual degradation of the scales through cuticle fragmentation. This process is related to the actual age or time the individual hair has been on the scalp (or its residence time) rather than to the chronological age of the individual and is described in detail in Chap. 6.

2.4 Chemical Composition of the Different Morphological Components

2.4.1 Cuticle

Bradbury et al. [17] suggested that the cuticle of human hair contains more cystine, cysteic acid, proline, serine, threonine, isoleucine, methionine, leucine, tyrosine, phenylalanine, and arginine than whole fiber. Data calculated from Bradbury's results and those of Robbins [13] on whole human hair fibers are summarized in Table 2.7. Wolfram and Lindemann et al. [69] described comparative cuticle and cuticle-free hair analyses of certain amino acids in human hair and their data are qualitatively similar to those of Bradbury [17] (see Table 2.7). In addition, these authors suggested less tryptophan and histidine in cuticle than in whole fiber.

In general, these results show that cuticular cells contain a higher percentage of the amino acids that are not usually found in alpha-helical polypeptides than is found in whole fiber. Small amounts of citrulline (11 μmol/g) have been reported in whole human hair fibers, whereas cuticle is found to be somewhat richer in citrulline (45 μmol/g) with only trace quantities of ornithine (5 μmol/g) [17].

The three major layers of the hair cuticle, A-layer, the exocuticle and endocuticle, have been separated after enzymatic digestion and analyzed [72]. Their chemical compositions are quite different and are described next.

Table 2.7 Amino acid composition of the different morphological components of hair[a]

Amino acid	Cuticle[b]	Whole fiber[c]	Medulla[d]
Aspartic acid	287	449	470
Threonine	524	664	140
Serine	1,400	1,077	270
Glutamic acid	819	1,011	2,700
Proline	994	667	160
Glycine	611	485	300
Alanine	–	374	400
Half-cystine	2,102	1,461	Trace
Valine	634	499	320
Methionine	38	53	40
Isoleucine	184	249	130
Leucine	418	516	700
Tyrosine	132	184	320
Phenylalanine	91	142	–
Cysteic acid	68	29	–
Lysine	–	217	740
Histidine	–	71	100
Arginine	360	529	180
Ammonia	–	–	(700)
Citrulline	45	11	–

[a]Data are expressed in micromoles amino acid per gram dry hair
[b]The data for cuticle analysis are based on the work of Bradbury et al. [17] who analyzed cuticle and whole fiber from several keratin sources, including human hair, merino wool, mohair, and alpaca. These scientists concluded that there is very nearly the same difference between the amino acid composition of the cuticle and each of these fibers from which it was derived. They listed the average percentage differences used in these calculations. More recent analyses of cuticle and whole fiber of human hair [69, 70] are in general agreement with these data [17]
[c]Whole-fiber results approximated by cortex analysis [13]
[d]These data are results of analysis of medulla derived from porcupine quill from Rogers [71]

2.4.1.1 A-Layer

The A-Layer was first discovered and named by Rogers [71] in 1959. It lies immediately beneath the epicuticle cell membrane. It is of relatively uniform thickness (~110 nm). Varying data have been published about its composition due to contamination arising from the difficulty to separate it from adjacent layers of the fiber, the cell membrane and the exocuticle. Swift [73] reported a very high half cystine content for the A-layer at approximately one half-cystine in every 2.7 amino acid residues or about 37 mol% half cystine an exceedingly high cystine content.

The A-layer is the most highly cross-linked region of the hair fiber being cross-linked by both cystine (disulfide) bonds and isopeptide (amide) groups formed between glutamine and lysine by a transglutaminase enzyme [74]. Isopeptide cross-links (sometimes called isodipeptide) are verified by the resistance of the A-layer to solubilization by reaction of a reducing agent (generally a mercaptan) in the

presence of a detergent solution. Generally, most proteinaceous systems that are cross-linked by disulfide bonds alone are readily solubilized by such a medium, but proteinaceous tissues that are cross-linked by isopeptide bonds are not readily dissolved by a reducing medium [75]. Furthermore, isopeptide bonds are also resistant to many enzymes that readily attack peptide bonds.

In this author's opinion, the most reliable estimate for the amino acid composition of the A-layer is the one by Bringans et al. [76] summarized in Table 2.8. Bringans et al. isolated their A-layer by essentially dissolving the rest of the fiber from it. They took Merino wool and scoured it, then solvent extracted it followed by methanolic KOH treatment to remove the MEA layer. The next step was to treat with reducing conditions using tris-2 carboxy ethyl phosphine followed by treatment with pronase E for 7 days. At various stages of treatment the sample was examined by TEM to estimate what structures were remaining in it. The composition of the remaining matter was largely A-layer containing only 3% lysine which at 50% conversion to isopeptide would provide only 1.5 mol% isopeptide bonding. This amount of isopeptide is somewhat lower than the estimate of 2.5 mol% suggested by Zahn et al. [77]. Bringans et al. [76] then digested the remaining A-layer with 2-nitro-5-thiocyano-benzoic acid to produce a large number of small peptide derivatives that were analyzed by mass spectrometry. A large proportion of the peptide derivatives fit the cuticular KAP 5 and KAP 10 families of proteins known to be in hair cuticle in large amounts. In addition, there was also strong homology to the KAP 4 and KAP 12 families of proteins. See the section entitled *The KAP Proteins of Human Hair* in this Chapter.

Table 2.8 Approximate composition of the A-layer from Merino wool by Bringans et al. [76]

Amino acid	A-Layer [76] mole%	Cuticle [76] mole%
Aspartic acid	1.3	4.2
Glutamic acid	5.2	8.1
Threonine	2.7	4.6
Serine	14.2	12.9
Proline	6.6	9.3
Glycine	18.4	9.8
Alanine	3.4	5.5
Valine	6.5	6.6
Isoleucine	2.0	2.7
Leucine	3.9	6.0
Half cystine + cysteic acid	25.1	14.7
Methionine	0.7	0.7
Tyrosine	1.1	3.7
Phenylalanine	1.6	2.1
Histidine	1.2	1.4
Lysine	3.0	2.9
Arginine	3.1	4.9

Table 2.9 Amino acid composition of exocuticle of wool fiber by Bradbury and Ley [78]

Amino acid	Mole percent
Aspartic acid	2.1
Glutamic acid	8.6
Threonine	3.9
Serine	11.9
Proline	12.4
Glycine	8.7
Alanine	6.4
Valine	8.2
Isoleucine	2.9
Leucine	4.6
Half cystine + cysteic acid	20.0
Methionine	0.2
Tyrosine	2.0
Phenylalanine	1.2
Histidine	0.5
Lysine	2.1
Arginine	4.8

2.4.1.2 Exocuticle

Bradbury and Ley [78] provided an amino acid analysis of exocuticle derived from physically isolated cuticle cells of wool fiber after pronase and trypsin digestion. This approach provided 20% cystine, about 10% acidic amino acids, about 7% basic amino acids and about 44% non-polar amino acids, see Table 2.9.

Swift [79] cited approximately 20% cystine in an exocuticle rich fraction from human hair, although the data showed a slightly higher amount which Swift attributes to exocuticle plus A-layer [72, 79]. Swift [72, 79] also indicated that the exocuticle likely contains virtually no isopeptide cross-links because of its rapid digestion in dithiothreitol/papain mixture, a medium that only slowly attacks the adjacent A-layer of hair. The exocuticle has been described by Swift as varying from 100 to 300 nm thick [73, 79] within the same cuticle cell and it averages about 200 nm thick.

The sequences of three mid-cuticle proteins have been described by M.L. Rogers et al. in several different publications and these contain about 20–22% cystine [80].

2.4.1.3 Endocuticle

The endocuticle of human hair has been shown by Swift [79] to be irregular in shape and varies from about 50 to 300 nm thick and averages about 175 nm. Relatively similar amino acid compositions have been reported for endocuticle from wool fiber by Bradbury and Ley [78] and from human hair by Swift and Bews [72], see the data of Table 2.10.

Swift and Bews [72] isolated three chemically distinct protein fractions all of low cystine content. These proteins were all easily digested by protease systems not

Table 2.10 Amino acid composition of hair and wool endocuticle

Amino acid	Endocuticle of hair [72]	Endocuticle of wool [78]	Averages
Aspartic acid	9.3	7.4	8.35
Glutamic acid	12.3	10.3	11.3
Threonine	5.9	5.5	5.7
Serine	10.3	10.7	10.5
Proline	7.3	8.9	8.1
Glycine	6.9	8.2	7.55
Alanine	5.9	6.7	6.3
Valine	6.5	7.5	7.0
Isoleucine	4.1	3.9	4.0
Leucine	8.7	9.3	9.0
Half cystine + acid	5.7	3.1	4.4
Methionine	1.5	0.8	1.15
Tyrosine	3.4	3.6	3.5
Phenylalanine	2.4	3.9	3.15
Histidine	1.0	1.1	1.05
Lysine	4.1	4.2	4.15
Arginine	4.8	5.0	4.9

containing reducing agents suggesting a lack of or relatively low levels of both disulfide and virtually no isopeptide cross-links. The low level of cross-links and the relatively high levels of polar (acidic and basic) amino acid residues suggest that this layer of cuticle cells is the one most prone to a high degree of swelling in water.

Thus, the proteins of the exocuticle and its A-layer are highly cross-linked by cystine (more than 30% combined exocuticle and A-layer) and therefore extremely tough and resilient. In contrast, the proteins of the endocuticle contain very little cystine (~3%) and relatively large amounts of the dibasic and diacidic amino acids.

As a result of these large compositional differences in the A-layer, exocuticle and the endocuticle, the cuticle can be expected to react differently to permanent waves, bleaches, and even to water and surfactants. Roper et al. [81] described a method to determine the cuticle composition from endocuticle of chemically treated wools. Such a procedure should be useful to evaluate changes in the endocuticle of cosmetically modified human hair.

2.4.2 Proteins of the Cell Membrane Complex

The structures of the three different types of cell membrane complex (CMC) are described in Chap. 1 in the section entitled, *Structure of the Three Different Cell Membrane Complexes*.

The schematic of Fig. 1.44 depicts cell membrane proteins and multiple layers of proteins in the Delta layer of the cuticle-cuticle CMC analogous to the Delta layer of the cortex-cortex CMC depicted in Fig. 1.45 [82, 83]. The structures and

composition of the proteins of the CMC are still not adequately characterized. The reason for this gap is that it is extremely difficult to isolate proteins from only the cell membranes or only the Delta layer. This difficulty has been the primary obstacle to our understanding the composition and structure of the proteins of this important region of the fiber. Much more scientific attention has been given to the analysis of cuticle cell membranes than to those of the cortex therefore I will begin this discussion on the proteins in the cuticle cell membranes.

2.4.2.1 Proteins in the Cuticle Cell Membranes

The proteins of the cuticle cell membranes are associated with the Allworden reaction [84] as described earlier. The membranous epicuticle supports 18-MEA and is attached to the A-layer on the top of cuticle cells and has been isolated by shaking animal hair fibers during Allworden sac formation and subsequently analyzed for amino acids. Perhaps the most quoted and "reliable" amino acid analysis of the Allworden membrane has been provided by Allen and coworkers [85] and is summarized in Table 2.11. The proteins in the cuticle cell membranes are described in detail in Chap. 1 in the section entitled *The Structures of the Three Different Cell Membrane Complexes*, where these leading references are cited [84, 85, 87–96]. See that section and those references for details.

Table 2.11 Amino acids from the proteins exracted from wool with performic acid [86] vs. Allworden membrane [85]

Amino acid	Allworden [85]	Resistant membranes [86]
Asp	3	5.4
Glu	8.6	10.3
Thr	2.1	5.7
Ser	14.3	10
Tyr	0	0
Pro	4.2	7.1
Gly	23.8	14.2
Ala	3.2	6.5
Val	5.6	4.9
Iso	1.2	2.6
Leu	2.9	4.9
Trp	–	0
Phe	0.4	1.5
His	0.2	1.3
Lys	4.5	8.4
Arg	2.5	4.2
Met	0	0
Cys	21.1	13
Totals	97.6	100

2.4.2.2 Proteins in the Cortical Cell Membranes

Proteinaceous material called "resistant membranes" have been isolated from both the oxidation of wool and or hair with performic or peracetic acid followed by treatment with either ammonia or alkaline urea [86]. The authors of this paper state that this material from the performic acid reaction is similar to their own analysis of Allworden membrane. However, both are clearly different from the Allworden membrane analysis by Allen et al. [85] as summarized in Table 2.11.

Treatment of keratin fibers with either peracetic or performic acid and separation into three fractions according to solubility has been called the "keratose" method by Alexander and Earland [97]. Some additional material on this method is described later in this Chapter in the section entitled, *Other Fractionation Methods*. After oxidation, adjustment of the pH to the alkaline side provides an insoluble fraction called Beta-keratose, about 10% of the weight of the hair. Acidification to pH 4 provides a fraction greater than 50% of the material called Alpha-keratose containing crystalline material, by x-ray diffraction. The third fraction called Gamma-keratose is believed to be largely from the matrix. The Beta-keratose fraction is believed to be proteins derived primarily from cell membrane material; however other proteins are likely present. According to a different workup procedure by Bradbury, Leeder and Watt [86], only 1–1.55% residue is provided. Other workup procedures have been applied to the keratose method [98].

Since the cell membrane lipids of cortical cells are not bound by thioester linkages as in cuticle cells, but by polar and ionic bonds, then no UHSP is necessary for the cell membrane proteins of cortical cells, but proteins with an adequate number of basic sites such as amino and guanidino (for bonding to cholesterol sulfate and to fatty acids) and polar sites such as carboxyl and hydroxyl groups would also be preferred for polar bonding to fatty acids and hydroxyl groups. The cortical cell membranes will most likely be resistant to oxidation, reduction and to acids and alkalies. Therefore, isopeptide bonds will be necessary and these could be formed by proteins such as involucrin and small proline rich proteins that are rich sources of glutamine to react with lysine groups of other proteins as in stratum corneum and in the cuticle cell membranes [85].

The resistant membrane material from the reaction of performic acid on wool fiber by Bradbury, Leeder and Watt [86] provides only about 62% of the amount of cystine as the composition of the Allworden membrane by Allen et al. [85]. It also contains about twice the basic amino acid content and basic amino acids are necessary to form salt linkages to cholesterol sulfate and carboxyl groups of fatty acids to form bilayers for cortical cell membranes. Performic acid derived membrane matter should be richer in cortical cell membranes, since they are a higher percentage of the total membrane matter in keratin fibers. However, other protein contaminants could be from the A-layer and cuticle cell membranes which also contain isopeptide bonds.

A cleaner experimental scheme to isolate pure cortical cell membranes would be to start with pure cortex to exclude cuticle cell membranes and A-layer proteins. Pure cortex from human hair could be provided by the glass fiber method of

Wortmann et al. [99] and then perhaps employ the performic acid reaction or another scheme to provide cortical cell membranes in the absence of cuticle contamination for further workup and analysis.

2.4.2.3 Proteins Extracted from Hair/Wool Believed to be from the CMC

Leeder and Marshall [100] extracted Merino wool with formic acid and also with n-propanol/water (50/50). Proteinaceous matter was removed from the hair fibers with each of these solvent systems. With formic acid, these scientists concluded that the proteins were at least partially derived from the CMC, most likely the Delta layer because the extract contained virtually no cystine. If this proteinaceous material is from the Delta layer it most likely is not from the central proteins, called the contact zone, because Naito et al. [101] provided evidence that the central contact zone contains hydrophilic protein with disulfide bonding.

Leeder and Marshall [100] concluded that the proteins derived from their propanol/water extraction of wool is not entirely from the cell membrane complex, but these proteins also contain high glycine-tyrosine proteins possibly from the cortex. The amino acid compositions of proteins extracted by formic acid, by n-propanol/water and by chloroform/methanol are compared with that of Allworden membrane in Table 2.12.

Logan et al. [102] demonstrated that a chloroform-methanol azeotropic mixture provides a very different mixture of proteins than the high temperature propanol/

Table 2.12 Proteins extracted from wool with formic acid and n-propanol water compared with Allworden membrane

Amino acid	Allworden [85]	Formic acid [100]	n-Propanol [100]	CHCl3/MeOH [102]
Asp	3.0	5.7	3.7	6.2
Glu	8.6	7.2	2.4	7.5
Thr	2.1	3.8	3.2	5.1
Ser	14.3	8.1	11.7	13.3
Tyr	0	12.0	16.4	3.0
Pro	4.2	4.0	5.2	6.4
Gly	23.8	19.2	25.0	11.9
Ala	3.2	5.2	2.2	8.0
Val	5.6	4.2	2.8	5.9
Iso	1.2	3.3	0.8	3.5
Leu	2.9	9.2	6.1	8.1
Trp	0	0	–	–
Phe	0.4	5.2	7.8	3.6
His	0.2	1.2	0.7	1.0
Lys	4.5	4.0	0.8	2.7
Arg	2.5	6.2	5.2	4.1
Met	0	0.9	0.2	0.8
Cys	21.1	0.4	5.5	9.0
Totals	97.6	99.8	99.7	100.1

water extraction, see Table 2.12. Could this chloroform-methanol extract be partially derived from cortical cell membranes or part of the outer lamella (outermost layer) of the Delta layer proteins of the CMC? Since Mansour and Jones [103] demonstrated that chloroform/methanol provides large changes to the cortex-cortex CMC in wool, it is likely that the proteins removed by chloroform/methanol are at least partially attached to Beta layers and are at least in part Delta layer proteins of the cortex-cortex CMC.

The method of Swift and Holmes [104] has been used by several different researchers to obtain proteinaceous matter believed to be partially derived from the CMC. This method involves dissolving matter from hair using papain with a reducing agent such as bisulfite or dithiothreitol (DTT). Bryson (Bryson W. Private communication) conducted a series of experiments from which he concluded that the laminated structure observed under the TEM following a 72 h digestion of wool fibers with papain and reducing solution (somewhat standard procedure) is not derived entirely from the CMC. Prolonging the digestion beyond 72 h increased the number of laminated layers beyond what could be accounted for by the number of cortical cells in a fiber cross-section. Bryson concluded that the CMC lipids were rearranging with other proteins and peptides to form these laminated layers.

Mass spectrometric analysis of the proteins of the digestion residue indicated that the majority of the protein component was papain, suggesting that the CMC lipids had rearranged with papain to form the laminated structures. Therefore, Bryson concluded it is not possible to isolate pure proteinaceous CMC by papain digestion. These conclusions by Bryson are consistent with those of Swift and Bews [72] who concluded that although treatments of keratin fibers with enzymes and reducing agents do cause separation of cells they could find no evidence of dissolution of the cuticle CMC via critical electron microscopic examination of treated hair sections. Therefore the value of this method for isolation of CMC proteins is limited because of contamination with papain.

2.4.3 Lipids of the Cell Membrane Complex

2.4.3.1 Methods to Remove Lipids from Animal Hairs for Analysis

To remove external lipids, wool fibers are normally cleaned by scouring with a nonionic agent such as Lissapol and then in scientific studies treated with one or more solvents to remove any remaining external lipids. Non-swelling and/or solvents of bulky molecules (like t-butyl alcohol [105]) have been used to remove external lipids from keratin fibers, that is, lipids that are believed to be soil and not part of the structural lipids of animal hairs. Solvents such as hexane, t-butyl alcohol or heptane and sometimes t-butanol and heptane sequentially [102, 106] have been used to extract external lipids such as wool wax or sebaceous matter from animal hairs. Such lipids are sometimes called external, extrinsic or even exogenous [107] and are not believed to be involved in the intercellular structure of animal hairs.

In the case of human hair, external lipids have been removed by shampoo or sodium lauryl sulfate washing, the safest procedure, or by a combination of shampoo followed by incubation in hexane for only 5 min [107] or in some cases other non-swelling solvents like ether or heptane which most likely do not remove significant amounts of internal hair lipids.

2.4.3.2 Removal of Internal Lipids Not Covalently Bound to Hair

Hair-swelling organic solvents alone or in combination with a second lipid solvent are used to remove internal lipids that are part of the internal structure of hair fibers (of the CMC) but not covalently bonded to hair protein structures. Swelling solvents such as chloroform/methanol [102, 108], methanol [108], ethanol [104], formic acid [109], n-propanol/water [109] or acetone [108] have been used to extract internal matter from animal hairs. The most frequently used solvent for removal of internal lipids has been chloroform/methanol (70/30) although other mixtures have been used. Normally soxhlet extraction is employed; however, multiple room temperature extractions have also been used [107]. Although formic acid and n-propanol/water (generally 1:1) do remove some internal lipids these two solvents also remove some hair proteins of the CMC (most likely from the Delta layers and possibly from other regions of the fibers see the section entitled, *Proteins of the CMC*).

2.4.3.3 Removal of Covalently Bound Hair Lipids Plus Salts Insoluble in Lipid Solvents

Alkaline hydrolysis or methanolic alkali is used to remove covalently bound hair lipids. This technique can be used to remove total hair lipids, but is generally used after extraction of external and internal lipids that are not covalently bound to the fibers. Those covalently bound lipids at or near the fiber surface are generally removed with potassium t-butoxide in t-butanol (bulky cleaving agent in a bulky solvent) [110]. Total covalently bound lipids are generally removed with potassium hydroxide in methanol because alkali in a swelling organic solvent like methanol penetrates well into hair.

In addition to covalently bound lipids, Wertz [111] suggested that salts of cholesterol sulfate bind ionically to cationic groups of the hair proteins and will be insoluble in chloroform/methanol. Therefore these ionically bound hair lipids will remain in the fibrous residue after extraction with organic solvents. Korner et al. [112] used a solution of chloroform/methanol/aqueous potassium chloride to extract CMC lipids from wool and human hair.

2.4.3.4 Total Lipids in Hair Fibers

The total amount of lipid extractable from hair is generally 1–9% of the weight of the hair [107, 113]. Masukawa et al. [107] studied the total hair lipid composition

from 44 Japanese females ages 1 to 81. The lipids were extracted/removed from hair in varying procedures to allow for analysis of several lipids and covalently bound 18-MEA. Total fatty acids and 18-MEA were determined, but other important fatty acids both covalently bound and non-covalently bound were not quantitated such as palmitic, stearic, oleic and palmitoleic acids which have been found in significant quantities in other studies [102, 111, 114–116]. Cholesterol sulfate was also not determined in this effort by Mazukawa et al.

Logan et al. [102] analyzed human hair by extracting it with a chloroform/methanol azeotrope for 5 h after surface lipids had been removed with t-butanol and heptanes. These scientists found 23% palmitic, 25% palmitoleic, 4% stearic, 13% oleic and other fatty acids. These are all non-covalently bound fatty acids with 39% of the total fatty acids being unsaturated (primarily palmitoleic and oleic). Although, it is possible other unsaturated fatty acids were present. Weitkamp et al. [117] analyzed solvent extracted lipids from pooled adult Caucasian human hair clippings and found 51% of the total fatty acids to be unsaturated with palmitoleic and oleic acids as the principal unsaturated fatty acids. However, other unsaturated fatty acids were found in these extracts.

Masukawa et al. [107] initially shampooed the hair and then washed it with hexane allowing a 5 min incubation time. The hexane wash was determined by plotting the amount of lipid extracted vs. the square root of time of the hexane wash. The time that diffusion of lipids from the interior of the fiber began was determined graphically, a reasonable approach to removing external lipid soils from the fibers and leaving most of the internal and structural lipids in the hair.

Mazukawa et al. then removed the hair lipids by extraction with different ratios of chloroform-methanol and separated them into eight groups; their data are summarized in Table 2.13. These data show that approximately 58% of the total lipids removed from hair under these conditions are fatty acids, some are covalently bonded, but others exist as free and non-covalently bound fatty acids. The total fatty

Table 2.13 Lipids in human hair from Masukawa et al. [107] and Wertz and Downing [115]

Type of lipid	mg/g hair		Percentage of total lipid	Source[a]
Hydrocarbons	2.4		9.7	U
Squalene	0.7		2.8	S
Wax esters	4.9		19.8	S
Triglycerides	0.5		2.0	S
Total fatty acids	14.4		58.1 [97][b]	S
Total covalent F. acids	–	(4.0)[c]		M/S
Cholesterol	1.3	(0.6)[c]	5.2	M
Cholesterol sulfate	–	(2.9)[c]		M
Ceramides	0.29	(0.5)[c]	1.2	M
18-MEA	0.30	(1.6)[c]	1.2	M
Totals	24.79		100%	

[a]Sources: U = Unknown; S = Sebaceous Glands; M = Hair Matrix Cells
[b]See Logan et al. [102, 118] for a breakdown of the actual fatty acids in human hair
[c]Data in parenthesis by Wertz and Downing [115], not in parenthesis by Masukawa et al. [107]

acids found were 14.4 mg/g of hair, but only 0.3 mg/g hair of 18-MEA were found. Wertz and Downing [111] found 1.31–2.1 mg/g of 18-MEA in four different human hair samples (three from individuals and one pooled hair sample presumably Caucasian hair). In a later paper, Wertz and Downing [115] cited 4.0 mg/g total integral (covalently bound) fatty acids with 40.5% as 18-MEA for human hair or 1.6 mg/g 18-MEA. Since most 18-MEA estimates in wool fiber are close to 1 mg/g or higher and human hair contains more cuticle layers than wool fiber one would expect more covalently bound fatty acids in human hair than wool fiber. Masukawa did not list amounts for total covalently bound fatty acids only 18-MEA. Therefore I listed and used the data for Wertz and Downing [115] for total covalently bound fatty acids.

2.4.3.5 Lipids of the Cuticle-Cuticle Cell Membrane Complex

Wertz and Downing [115] examined five different mammalian hairs from sheep, humans, dog, pig and cow and found the percentage of 18-MEA relative to the total amount of covalently bound fatty acids varied from 38% to 48%. Table 2.14 summarizes a tabulation of analyses of the covalently bound lipids of wool and human hair from several different laboratories. These results were all obtained after the fibers had been exhaustively extracted with chloroform/methanol to remove the non-covalently bound fatty acids and then the residue saponified with methanolic alkali showing that 18-MEA accounts for about 50% of the covalently bound fatty acids in these wool fibers and about 40% in human hair.

2.4.3.6 Covalently Bound Internal Lipids of Animal Hairs

Korner and G. Wortmann [119] (Table 2.14), analyzed covalently bound fatty acids in isolated wool cuticle and found 55% 18-MEA, 25% stearic and 20% palmitic acid with "only traces of other straight and odd number carbon chain fatty acids."

For wool fiber Wertz and Downing [115] found 48% 18-MEA and 17% palmitic acid, 10% stearic acid, 5% oleic acid and the remaining covalently bound fatty acids ranged from C16 through C20 with 6% uncharacterized. For human hair, Wertz and Downing [111] found 41% 18-MEA, 18%, palmitic acid, 7% stearic acid, 4% oleic

Table 2.14 Covalently bound fatty acids in wool and human hair fiber

Fatty acid	Data for wool fiber						Data for human hair
	[114]	[118]	[116]	[115]	[119]	Averages	[111]
16:0	8	11	8	17	20	12.8	18
18:0	8	12	6	10	25	12.2	7
18:1	7	8	5	5	0	5	4
MEA	51	43	72	48	55	53.8	41
Others	26	26	9	20	Trace	16.4	30

Data are expressed in percentages

acid and the remaining small percentages of fatty acids from C16 through C20 with 9% uncharacterized. Negri et al. [116] found 72% 18-MEA, 8% palmitic acid, 6% stearic acid and 5% oleic acid in wool fiber.

The variation in these data from different laboratories is quite large. Part of the variance has been suggested to be related to fiber diameter which determines the number of layers of covalently bound fatty acids in the fibers. However, certainly part of the variance is due to experimental error. The bottom line is that somewhere in the vicinity of 50 ± at least 10% of the covalently bound fatty acids in most keratin fibers is 18-MEA and that hair fibers from sheep, humans, dog, pig and cattle and likely most keratin fibers contain palmitic, stearic and oleic with other fatty acids as the remaining covalently bound fatty acids.

In 1990, Kalkbrenner et al. [120] demonstrated with isolated cuticle cells that 18-MEA is essentially all in the cuticle. 18-MEA represents more than 40% of the total covalently bound fatty acids in human hair and about 50% in wool fiber. 18-MEA is confined to the upper Beta layer of the cuticle [121, 122] while most (essentially an amount equal to the 18-MEA) of the other covalently bound fatty acids are confined to the lower Beta layer. Therefore, most of the covalently bound fatty acids in wool and hair fiber must be in the cuticle-cuticle CMC with some in the cuticle-cortex CMC (to be described later) and virtually none in the cortex-cortex CMC. So, if most of the covalently bound fatty acids are in the cuticle-cuticle CMC, then most of the lipids of the cortex-cortex CMC must be bound to the membranes on one side and to the Delta layer on the other by non-covalent bonds. The fact that most of the remaining lipids can be removed by solvent extraction confirms that this is the case.

Leeder, Bishop and Jones [123] first found that there are virtually no phospholipids in keratin fibers. This fact was confirmed by Schwan and Zahn [124] and by Rivett [125] casting doubt on whether lipid bi-layers could be involved in the cell membranes of keratin fibers [123]. However, Wertz et al. [126] demonstrated that liposomes (lipid bi-layers and a presumed precursor to the formation of lipid bi-layers in the CMC of keratin fibers) can form in the absence of phospholipids if an acid species such as cholesterol sulfate is present with other lipids. Furthermore, evidence has been provided confirming the existence of cholesterol sulfate in human hair by Wertz and Downing [111] and by Korner et al. in wool fiber [112].

The work of Korner et al. [112] builds upon the findings of Wertz et al. on liposome formation and lipids from stratum corneum [126]. Korner et al. [112] demonstrated that cell membrane lipids extracted from human hair and wool fiber with chloroform/methanol/aqueous potassium chloride can form liposomes. This result provided evidence for a bi-layer structure of the internal lipids of the Beta layers of the cortical CMC in wool fiber and in human hair, see Fig. 1.45. Such extracts must come primarily from the cortex-cortex CMC because covalently bound MEA and the other covalently bound lipids of the cuticle CMC are not removed with this solvent system.

Therefore, if the Beta layers of the cuticle cells are primarily covalently bound fatty acids with some free lipids (see Fig. 1.44) and the Beta layers of cortical cells

consist primarily of lipid bi-layers (Fig. 1.45), then it is highly likely that the proteins that these very different lipid layers are attached to are also different. These proteins are the cell membrane proteins and the Delta layer proteins of the cuticle cells and the cortical cells, see the section on *Proteins of the CMC* and the next section of this Chapter.

2.4.3.7 Lipids of the Cortex-Cortex Cell Membrane Complex

Since Mazukawa et al. [107] found 14.3 mg/g total fatty acid, but did not determine the total covalently bound fatty acids, and Wertz and Downing found 4 mg/g total covalently bound fatty acids then the Mazukawa et al. data most likely represents or is closer to the total amount of non-covalently bound fatty acids in human hair. So, if we assume human hair has approximately 14 mg/g of non-covalently bound fatty acids and about ½ the equivalent amount of free lipid in the cuticle relative to covalently bound fatty acid. This provides 2 mg/g free fatty acid in cuticle layers, leaving about 12 mg/g of non-covalently bound fatty acids. If we assume 2 mg/g fatty acid as intracellular lipid that leaves 10 mg/g fatty acids in the cortex-cortex CMC. So, with these approximations, about 10 mg/g of fatty acids will exist in the "bi-layers" of the CMC of the cortex, along with cholesterol, cholesterol sulfate and ceramide (see Fig. 1.45).

Wertz and Downing [115] found cholesterol (0.6 mg/g), and cholesterol sulfate (2.9 mg/g) and ceramides (0.5 mg/g) in their alkaline hydrolysates from human hair after removal of all free lipids by chloroform-methanol extraction. These same scientists also found these same lipid components in hair from sheep, dog, pig, cow and humans varying from (0.3 to 1.4 mg/g) cholesterol, ceramides (0.6 to 1.4 mg/g) and cholesterol sulfate (0.7 to 3.3 mg/g) [115].

Examination of these data from different laboratories suggests the following ingredients in these approximate ratios as the principal components of the bi-layers of the cortex-cortex CMC for human hair:

Lipid component	Approximate amount	Approximate relative amounts
Fatty acids	10 mg/g hair	10
Cholesterol sulfate	0.7–3.3 mg/g	2
Cholesterol	0.6–1.2 mg/g	1
Ceramides	0.6–1.4 mg/g	1

These ratios are clearly not exact, but they show a large amount of fatty acid followed by cholesterol sulfate and smaller amounts of cholesterol and ceramide.

2.4.3.8 Lipids of the Cuticle-Cortex Cell Membrane Complex

If the cuticle-cortex CMC is a hybrid of the cuticle-cuticle CMC and the cortex-cortex CMC the composition of the lipids and the proteins should be essentially a 50/50 mixture of the proteins of the cuticle-cuticle CMC and the cortex-cortex CMC.

2.4.3.9 Lipids of the Surface

These lipids are essentially those covalently attached to the epicuticle such as 18-MEA and those free lipids that are associated with 18-MEA and the epicuticle proteins.

2.4.3.10 After Shampooing an Appreciable Amount of Free Lipid Remains in the Hair Surface

Shaw [127] suggested that washing hair with ether or shampoos in a one-step application leaves virtually the entire hair surface free of lipid and that differences in cleaning efficiencies of surfactants relate to the amounts of internal lipid removed. Recent XPS data show that shampooing does remove some free-lipid from the surface of hair, but even after shampooing an appreciable amount of free-lipid remains in the surface layers, that is in the top 3 nm [128].

2.4.3.11 Free-Lipid in Surface Layers Affects Isoelectric Point of Wool and Hair

Capablanca and Watt [129] examined wool fiber that had been washed with detergent (Lissapol) and extracted with various solvents using a streaming potential method to estimate the effect of free-lipid (including non-covalently bound fatty acids) in the surface layers on the isoelectric point of wool fiber. These scientists found an appreciable effect of free-lipid on the isoelectric point. The surfactant washed wool (containing the most free-lipid) provided an isoelectric point of 3.3. The isoelectric point of wool increased as the effectiveness of the solvent system increased with the most effective lipid solvent providing an isoelectric point of 4.5.

These data show that free fatty acids in the surface layers are an important and essential component of the surface of animal hairs and about half of the free lipid is fatty acid [130]. So, the more free-lipid present in these surface layers, the lower the isoelectric point of keratin fibers. Therefore, all free-lipid is not totally removed and should not be totally removed from the surface layers by shampooing of hair or scouring of wool fiber. In addition, free fatty acids are important to the isoelectric point of animal hair fibers. Furthermore, the amount of free-lipid in the surface of hair fibers will influence hair friction, surface energy and a whole range of important properties including the adsorption of surfactants and other ingredients onto human hair and wool fibers.

Hoting and Zimmerman [38] demonstrated that the cell membrane complex lipids of hair fibers are degraded more by visible light, but also by UV-A and by UV-B light, helping to explain the weakened cell membrane complex and the multiple step fractures observed in sunlight oxidized hair described in detail in Chap. 5. Obvious weak links to photochemical attack on lipid structures are the

allylic hydrogen atoms of unsaturated fatty acids and the tertiary hydrogen atoms of 18-MEA and other species. Hoting and Zimmerman also demonstrated that the cell membrane complex lipids of chemically bleached hair are more readily degraded by physical actions than the lipids of chemically unaltered hair. For example, longer term irradiation does not provide for clean breaks between structural components of hair as was observed for peroxide oxidized hair, see Chap. 5 for details. For more details on the structure of the CMC and the hair surface see the sections entitled *Epicuticle and the Hair Fiber Surface* and *The Cell Membrane Complex Including the Intercellular Non-keratin Regions of Hair* in Chap. 1.

2.4.3.12 Four Different Classes of Human Hair Lipids

There are at least four different but meaningful classifications of hair lipids. Hair lipids are described as free or bound, as endogenous or exogenous lipids, as internal or surface and by chemical functional group or chemical type.

Bound lipids are those that cannot be removed by extracting the hair with lipid solvents because they are covalently bonded to hair proteins. For example, 18-MEA is attached to proteins by thioester linkages, whereas free lipids are extractable from hair using lipid solvents because they are held by weaker bonding forces such as van der Waals attractive forces and sometimes hydrogen bonding or even salt links. Endogenous lipids are those hair lipids that result from biosynthesis in hair matrix cells in the hair follicle, whereas those lipids in the hair that are usually synthesized in sebaceous glands are sometimes called exogenous of an extrinsic source. Internal lipids are those that have either penetrated into the hair or have been incorporated inside the hair fiber as opposed to surface lipids. Chemical groups commonly used for this type of classification are similar to those described in the paragraphs below.

From the comprehensive study of hair lipids by Masukawa et al. [107] hair lipids were described in the section entitled, *Total Lipids in Hair Fibers*. In this study, hair lipids were extracted and analyzed from both the proximal and distal parts of the hair of 44 Japanese females between the ages of 1 and 81 and the composition determined quantitatively. These scientists separated the lipids into four groups by chemical type: Group A: Squalene (SQ), Wax esters (WE), Triglycerides (TG), and fatty acids (FA); Group B: cholesterol (CH) and ceramides (CER); Group C: hydrocarbons (HC) and Group D: 18-methyl eicosanoic acid (MEA). They also classified these lipids by source, for example those from sebaceous glands and those from hair matrix cells. These data are summarized in Table 2.13.

2.4.3.13 Bound and Free Lipids

The bound lipids are those lipids of the cell membrane complex that are covalently bonded to proteins including the 18-MEA attached to the epicuticle at the surface, described earlier in this Chapter and in Chap. 1. 18-MEA is part of a lipid monolayer surrounding each cuticle cell. 18-MEA is bound to the top of each cuticle

cell (and part of the scale edge) through thioester linkages [87]. 18-MEA forms the outer surface layer of the virgin hair surface as well as the top layer of each cuticle cell. The bottom of each cuticle cell and part of each scale edge is covered primarily with straight chain fatty acids that are mainly palmitic, stearic and other fatty acids including some oleic acid. These fatty acids are bound either through ester or thioester linkages to the underlying proteins. All other lipids that have been described in the literature are believed to be free lipids, that is, lipids that are not covalently bonded to hair proteins and they exist on and in the cuticle and the cortex. Additional details of covalently bound fatty acids are described in the section on the Cell Membrane Complex in this Chapter and in Chap. 1.

2.4.3.14 Surface Lipids of Human Hair

If we define the hair surface as the top 3–5 nm of the hair fiber, we find that 18-MEA is the primary lipid of that surface, but there is also free lipid in this surface too and there will likely be more free lipid in the surface the longer the time interval between shampooing and when lipid analysis is made. Evidence to support free lipid in the surface of hair stems from defining the hair surface as the top 3–5 nm and using x-ray photoelectron spectroscopy (XPS) to measure the C/N ratios in that surface. Estimates appear in Table 2.15 for the percentages of free lipid, 18-MEA, protein and total lipids in the outermost 3–5 nm of the fiber.

Some of the assumptions in these calculations are that the epicuticular proteins consist of 16.7% nitrogen and 45.3% carbon as calculated from the composition of CE proteins by Zahn et al. [88]. For 18-MEA, the carbon content is represented by

Table 2.15 Estimates of lipids and protein in the surface layers of hair fibers as a function of washing and treatment

Treatment	% Protein	% MEA	% Free lipid	Calc C/N	Found C/N	Total lipid
Wool Soxhlet $CHCl_3$:MeOH [131]	53.7	46.3	0[a]	6.9	6.9	46.3
Roots dei water[b] 18″ cut at scalp [6]	16.2	35.6	48.2	26.8	26.7	84
Tips dei water[c] 18″ cut at scalp [6]	23.2	18.1	58.7	17.9	18.0	77
Hair rinsed[d] dei. Water [6]	35.3	44.2	20.5	11.4	11.4	65
Hair washed[e] SLS [6]	44.0	44.2	11.8	8.8	8.8	56

[a]Sulfur VI assumed to be 20% Ward et al. scoured their wool with surfactant and then Soxhlet extracted it with a 2:1 $CHCl_3$: MeOH solvent therefore the free lipid content was assumed to be 0% and the Sulfur VI was assumed to be 20%, close to the value found by Carr et al. [132]
[b]Sulfur VI = 38.6%
[c]Sulfur VI = 68.8%
[d]Sulfur VI = 23.7%
[e]Sulfur VI = 23.7%

the acyl group without the sulfur because the sulfur is part of the protein structure. Therefore, the % carbon of 18-MEA is 81.6% and 75% carbon formerly used for the free lipids as suggested by Carr, Leaver and Hughes [132] from the work by Rivett et al. [133].

Carr, Willis St. John and George [132, 134] examined wool fiber by XPS in which the fibers had been Soxhlet extracted with chloroform/methanol. These scientists calculated that 18-MEA is approximately 1 ± 0.5 nm thick. This estimate is smaller than the length of the 18-MEA molecule which approaches 3 nm. Therefore, Zahn et al. [77] concluded that the 18-MEA chains fold back on themselves on the surface of keratin fibers to achieve the measured thickness of the lipid layer.

The data of Table 2.15 suggest that some free lipids are bound within the 18-MEA layer and as free lipids can be removed and then the 18-MEA chains fold back on themselves as suggested by Zahn et al. [77]. However, at higher free lipid levels there is less nitrogen and therefore less protein in the top 3–5 nm. Thus as more free lipid is incorporated within the 18-MEA layer it allows the 18-MEA chains to straighten out to accommodate the free lipid and to approach the expected length of 18-MEA (2.7–2.8 nm calculated by this author) and to occupy a higher percentage of the top 3–5 nm of the surface.

The data of Table 2.15 compares root ends vs. tip ends of hair more than 12 in. long (~30 cm) and cut directly from the scalp. This hair was not shampooed prior to XPS analysis, but only rinsed with deionized water. These data show very high free lipid levels in spite of the high oxidation level revealed by the SVI data showing 38.6% oxidized sulfur at the root ends and 68.8% oxidized sulfur at the tip ends. In spite of the high oxidation levels of this hair the free lipid levels are also high because of the accumulation of free lipids in or on the surface and the lack of shampooing of the sample prior to analysis. This conclusion is confirmed by the data of this same Table showing the effects of shampooing on the free lipid content of another hair sample.

The data of Table 2.15 also shows the effects of washing the hair with sodium lauryl sulfate on the surface lipids. Note, this hair was sampled near the root ends from another person who had a lower level of oxidized sulfur compared to both root and tip ends of hair described by the data in this same table. Washing the hair with sodium lauryl sulfate removed free lipids from the hair surface, but still left about 12% free lipids in the top 3 nm of the hair.

Capablanca and Watt [129] demonstrated that free lipids in the keratin fiber surface serve to lower the isoelectric point of wool (hair) and thereby affect the charge character of the surface. This free lipid could affect the binding of conditioner ingredients on and in the surface layers. Free lipids are also very difficult or virtually impossible to completely remove simply by shampooing or by means that are available to consumers. Thus, free lipids should be viewed as vital components of the hair fiber surface that are important for protection of the hair and to the interactions of conditioners and shampoos rather than as simply soil. For more details on the surface structure of human hair see the section in this Chapter entitled *Epicuticle and the Hair Fiber Surface*.

2.4.3.15 Free Lipids in the Total Hair Fiber

The data of Mazukawa et al. [107] (Table 2.13) demonstrated that fatty acids (~58%), wax esters (~20%) and hydrocarbons (~10%) comprise the major part of the free lipids in hair, almost 90% of the total lipid (free plus bound) in hair from a population of 44 Japanese females. These data are generally consistent with the types of free lipids found in the hair of Caucasian adults showing the largest amount as free fatty acids and the second largest amount as wax esters [135, 136].

A few years ago, Hussler et al. [137] isolated and identified low levels of ceramides in human hair lipid from Caucasians. Masukawa et al. identified these same ceramides as free lipids (~290 μg/g hair) at levels similar to those of 18-MEA by Masukawa et al. [~300 μg/g hair average at the proximal ends (470–220 μg/g variation among individuals)], but slightly higher than the levels found by Hussler and co-workers (~100 μg/g).

According to data by Nicolaides and Rothman [138] lipid extracted from human hair is similar but not identical to the composition of scalp lipid. However, cell membrane complex lipid is also partially removed by extraction of hair with lipid solvents or surfactants. In a sense, the scalp serves as a lipid supply system for the hair, with sebum being produced continuously by the sebaceous glands [139, 140]. Sebum production is controlled hormonally by androgens that increase cell proliferation in the sebaceous glands. In addition, seasonal and even daily variations in the rate of sebum production do occur [139].

The aging of the sebaceous glands in man is controlled primarily by endocrine secretions [139]. For children, sebaceous secretion is low until puberty, when a large increase in sebaceous activity occurs (see Fig. 2.2). Note, the data of Fig. 2.2 did not permit a plot of the entire age curve for females; however, the same general effect of low sebaceous activity for males and females before puberty does exist.

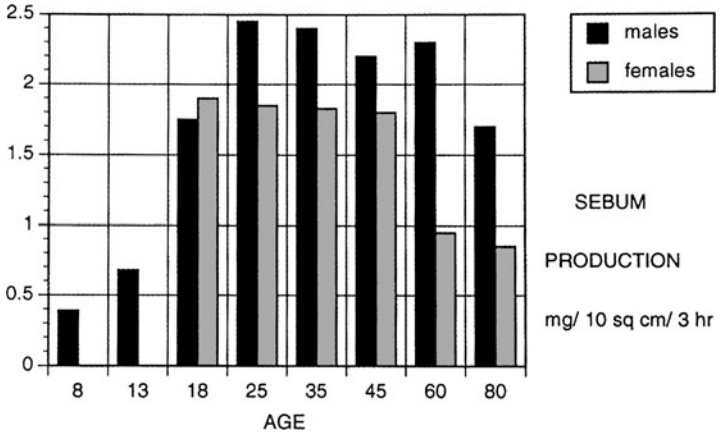


Fig. 2.2 Variation of sebum production on foreheads with age. Data are from Pochi et al. [141, 142]

For all ages, sebaceous-gland activity is lower for women than for men [139], and shortly before menopause (generally decreasing substantially in the mid-forties age range), there is a distinct decrease in sebum secretion, to even lower levels, see Fig. 2.2 and, *The effects of Menopause on the lipids in hair and on the hair fiber*. For males, there is more of a gradual reduction in sebum secretion with age beyond about 30 years. Strauss and Pochi [140–141] concluded that in both males and females, androgenic secretions are of primary importance for sebaceous-gland development and activity.

Extraction of human hair with "fat solvents" removes approximately 1–9% lipid matter. Ethanol, a solvent that swells hair, removes more material from hair than non-swelling solvents like benzene, ether, or chloroform. Hair consists of surface and internal lipid. In addition, part of the internal lipid is covalently bound and part is not covalently bound but both types of lipid can be cell membrane complex lipid. The cell membrane complex is laminar in structure and is composed of both protein and lipid layers; however, this structural lipid is not phospholipid [143, 144] like the lipids normally associated with bilayers of cell membranes (see the sections on *The Structures of the Three Different Cell Membrane Complexes* in Chap. 1 and additional parts of this chapter).

The data (1–9% extracted hair lipid) represent total matter extracted from hair clippings of individual men and women. Although the conditions for extraction can influence the amount of matter extracted from hair (Crawford R. Private communication), the values here represent "approximate" maxima and serve to indicate the variation in the amount of solvent extractable material from hair among individuals. Presumably, the principal material in these extracts consists primarily of free fatty acids (FFA) and neutral fat (esters, waxes, hydrocarbons, and alcohols). Gloor [145] classified the different components of sebum into six convenient groups: free fatty acids (FFA), triglycerides (TG), free cholesterol (C), cholesterol and wax esters (C & WE), paraffins (P), and squalene (S). These classes are similar but not identical to the classification groups by Masukawa et al. [107].

Spangler synthetic sebum (Table 2.16) provides a working formula to represent an imitation of average sebum. It contains lipid compounds to represent each of the six components of Gloor's classification for sebum. Nicolaides and Foster [146] examined ether extracts of pooled hair clippings from adult males and found 56.1% as FFA and 41.6% as neutral fat. In contrast, daily soaking of the scalps of adults

Table 2.16 Spangler synthetic sebum

Lipid ingredient	Percentage
Olive oil (TG)	20
Coconut oil (TG)	15
Palmitic acid (FFA)	10
Stearic acid (FFA)	5
Oleic acid (FFA)	15
Paraffin wax (P)	10
Squalene (S)	5
Spermaceti (WE)	15
Cholesterol (C)	5

Table 2.17 Composition of FFA in human hair lipid

Chain length	% Total FFA	% Unsaturated FFA of this chain length
7	0.07	–
8	0.15	–
9	0.20	–
10	0.33	–
11	0.15	–
12	3.50	4
13	1.40	3
14	9.50	15
15	6.00	25
16	36.00	50
17	6.00	67
18	23.00	80
20	8.50	85
22	2.00	–
Residue	4.00	–
Total	100.80	

(males) in ether provided 30.7% FFA and 67.6% neutral fat. Nicolaides and Rothman [138] suggested that this apparent discrepancy is likely from lipolytic hydrolysis of glycerides in the stored hair clippings.

Analysis of the FFA extracted from pooled hair clippings of adult males was conducted by Weitkamp et al. [117]. Their study did not contain data concerning the effect of lipolysis on the structures of FFA in hair fat. Saturated and unsaturated fatty acids ranging in chain length from 5 to 22 carbon atoms were found in human hair fat [117, 147]. Location of the double bond in the unsaturated acids is suggested to occur at the 6, 7 position, with some 8, 9 and other isomers. Data from the study by Weitkamp et al. [117] are summarized in Table 2.17. In addition to the acids reported by Weitkamp et al. [117], Gershbein and Metcalf [147] examined the total fatty-acid content (following saponification) of human hair fat and found traces of C5 and C6 carboxylic acid and small quantities of C19 and C21 acids, as well as branched-chain isomers of several other fatty acids [147].

Comparison of the FFA content [117] with the total (hydrolyzed) fatty acid content [148] is summarized in Table 2.18. This comparison assumes that data from different laboratories are comparable. With the exception of the C16 and C20 acids, the data in columns A and B of Table 2.18 are very similar for each corresponding acid. Equivalence suggests that the relative amounts of each acid in ester form would be the same as the relative ratios of the free acids, and that hydrolysis may occur on standing (or other conditions) to increase the ratio of FFA to esters. The noteworthy exceptions are the C16 saturated acid that must exist in ester form to a greater extent than suggested by the relative ratios of free acids and the C20 unsaturated acid, that was found only in trace quantities by Gershbein and Metcalf [147]. A further conclusion from these studies is that the principal acyl groups present in human hair lipids are from the C16 fatty acids.

Table 2.18 Comparison of FFA content of human hair with total fatty acid content

Chain length	% Total FFA [117]	% Total fatty acids [147]
12	3.36	2.19
13	1.36	–
14	8.10	8.40
15	5.50	6.70
16	18.00	24.90
17	2.00	2.30
18	5.00	4.60
20	1.30	–
Chain length	Relative ratio to C14 FFA	Relative ratio to C14 total fatty acids
12	0.4	0.3
13	0.2	–
14	1.0	1.0
15	0.7	0.8
16	2.2	3.0
17	0.3	0.3
18	0.6	0.6
20	0.2	–

Only those acids above 1% are listed

Analysis of some of the neutral material from human hair lipid, for example, triglycerides, cholesterol or wax esters, and paraffins provides a mixture as complex as that of the fatty acids [117, 138, 146, 149]. Although not all of the compounds of these different components of hair lipid have been fully analyzed, it is obvious from the discussion on fatty acids and the literature on wax alcohols in human hair lipid [117, 147, 149, 150] that the variation in chain length and isomer distribution of all of these esters must be extremely complex. The data of Table 2.18 compares the free fatty acid content of human hair with the total fatty acids from hydrolysis. These data show that C16 fatty acids are at the highest levels consistent with other data, but do not contain 18-MEA because these data are more than 40 years old.

It is well known that the amount of sebaceous secretion increases with age near puberty [139, 140]. The composition of the sebaceous secretion also changes at that time [151]. Nicolaides and Rothman [151] demonstrated that the paraffinic hydrocarbon content of sebum is highest in children (boys), lower in men, and lowest in women. These same two scientists also showed that the squalene content of the hair lipid of children is approximately 1.35% of the total lipid content and about one-fourth that of adults. Sebum from boys' age 6 to 12 was examined in this study and compared to that from both men and women. In addition, the cholesterol content of the hair lipid of adults is lower than that from children: 3.7% vs. 12.2% [151].

Nicolaides and Rothman [138] determined with small sample sizes that hair from African-Americans contains more lipid than hair from Caucasians. Gershbein and O'Neill [149] examined the distribution of fatty alcohols of human hair lipid to determine the relative amounts of fatty alcohols and sterols with regard to sex, race, and scalp condition. Samples originated from Caucasians and African-Americans,

both full haired and balding, and from Caucasian women. The data indicated essentially no differences among these parameters between the two racial groups or between the sexes. Kreplak et al. [152] examined lipid profiles in transverse cuts across hair using synchrotron infrared micro-spectrometry and determined that Caucasian hair often contains lipids localized inside the medulla and the cuticle, but it occurs to a lesser degree inside the cuticle. Further, the African-American hair that was analyzed does not show these same hair lipid effects across the section and is insensitive to solvent extraction.

Several other factors relevant to differences in sebum composition on the scalp have been described in the literature. Anionic surfactants or ether extraction of the scalp does not stimulate the rate of re-fatting [153, 154]. Selenium disulfide in a shampoo increases sebum production [154] and it alters the ratio of triglycerides to free fatty acids found in sebum. Presumably, this latter effect involves reducing the microflora responsible for lipolytic enzymes on the scalp that hydrolyze triglycerides to free fatty acids. Zinc pyrithione appears to behave similarly and has been shown to increase hair greasiness [155], presumably in an analogous manner. However, ketoconazole (another antifungal agent) behaves in the opposite manner. Pierard-Franchimont et al. [156] confirmed the increase in sebum excretion rate for selenium sulfide and further demonstrated that ketoconazole decreases sebum excretion.

Several studies demonstrated significant differences in the lipid composition of oily vs. dry hair. Perhaps the most comprehensive study in this regard was by Koch et al. [144], who examined hair surface lipid from 20 dry- and oily-haired subjects, 3 days after shampooing, and found the following correlations with increasing hair oiliness:

An increasing percentage of wax esters in the lipid,
An increasing ratio of unsaturated to saturated fatty acids,
An increasing amount of monoglycerides, and
A decreasing percentage of cholesterol esters with increasing oiliness.

The quantity of total lipid was not found by Koch to correlate with hair oiliness. However, this is not surprising (in a several-day study), because the quantity of lipid on hair tends to level after a few days from shampooing because of partial removal of excess lipid by rubbing against objects such as combs or brushes and even pillows and hats.

Koch et al. [144] explained oily vs. dry hair by the rheological characteristics of the resultant scalp lipid. For example, increasing the ratio of unsaturated to saturated fatty acids should decrease the melting point of the sebum, making it more fluid and thereby more oily. Monoglycerides are surface-active and therefore should enhance the distribution of sebum over the hair [144]. Factors such as fiber cross-sectional area or hair curliness were kept constant in Koch's experiments and thus not considered; however, one would expect the degree of oiliness to affect straight, fine hair the most and to have the least cosmetic effect on curly coarse hair [157].

Bore et al. [158] found that the structures of the C18 fatty acids of oily and dry hair differ. For subjects with dry hair, Bore et al. found the predominant isomer as octadecenoic acid (oleic acid), whereas for subjects with oily hair 8-octadecenoic acid was the predominant isomer. Thus oily hair is different from dry hair in its chemical composition and in its rheological character. Hair lipid plays a critical role in shampoo evaluation (Crawford R. Private communication) and in surface effects of hair, such as frictional effects [159]. See Chap. 6 for discussion of the removal of hair lipid by shampoos.

2.4.4 The Effects of Menopause on the Lipids in Hair and the Hair Surface

Wills et al. [160] showed that the cholesterol and ceramide (both matrix cell origin) content of the hair of pre-menopausal women was significantly higher while wax esters and squalene contents (both primarily from sebum) were significantly lower in post-menopausal women. These same authors noted that their analytical procedure could not distinguish between wax esters and cholesterol esters; however the wax ester levels are much higher in adult human hair than cholesterol esters as shown by the work of Pochi, Strauss and Downing [161].

Wills et al. [160] also found that the hair of pre-menopausal women (N = 80) was significantly greasier than the hair of post-menopausal women (N = 47). These scientists used expert visual assessment for this determination. In this same study, the hair of post-menopausal women on hormone replacement therapy (N = 39) was intermediate in greasiness and all three groups' scores were significantly different from each other. In addition, the amount of lipid found on the forehead of these same subjects was significantly higher in the pre-menopausal group than both of the other groups and the post-menopausal group not on hormone replacement therapy had the lowest amount of lipid (−57% vs. the pre-menopausal group). This effect is consistent with that of Pochi and Strauss [141, 161] who showed that hair on the foreheads of women decreased significantly in the mid-forties and has been attributed to the menopause.

Analysis of the amount of actual hair lipid by Wills et al. was on only 20 selected subjects of each group and proved to be not significantly different between the pre- and post-menopausal groups. These authors speculated that perhaps other factors such as "permeability of hair to sebum changes with menopause" or that the manner that the groups were balanced interfered with this determination.

The ages of these three groups were: pre-menopausal, mean age 30, range 24–34; post-menopausal, mean age 60, range 50–76; and post-menopausal with hormone replacement therapy, mean age 57, range 48–68. So, the prime variables are menopause and hormone replacement therapy, however there is also an additional factor of age especially between pre- and post-menopausal groups.

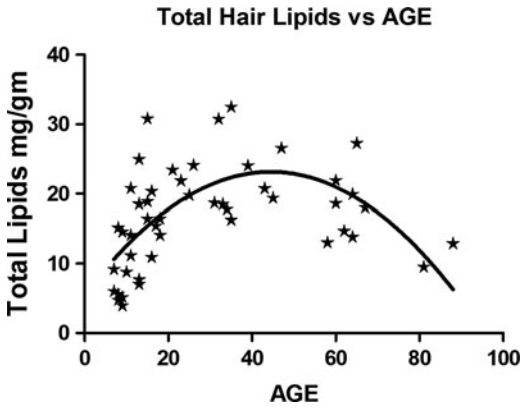


Fig. 2.3 Total hair lipid levels as a function of age. Data are from the P&G Wella Hair Research Group

Data for lipids on and in hair by age from an unpublished study by P&G/Wella Hair Research Group (see Fig. 2.3) shows a corresponding relationship to that found on foreheads by Pochi and Strauss [141] and by Wills et al. [160]. In this study, hair samples were collected from 51 Caucasian females varying in age from 7 to 88. This hair was extracted and analyzed by GC/MS (at the German Wool Research Institute (DWI)) for lipids. A Box plot of the Wella data revealed two outliers and the data was not normally distributed by the Shapiro-Wilk test (Shapiro-Wilk $W = 0.942$ and $p = 0.0147$). But, when these two outliers were rejected the data provided a normal distribution with a Shapiro-Wilk W of 0.978 and a $p = 0.5$ (very good). These normally distributed data when regressed vs. age provided a quadratic model with $p < 0.0001$, root mean square error of 5.623 and an r^2 of 0.387. From the model equation, the maximum for hair lipids was at age 45 corresponding to about where the steep drop occurs for sebum production on the foreheads of women by Pochi and Strauss [141] of Fig. 2.2. The age 45 peak appears to be influenced by the peri-menopause and is consistent with the work and conclusions of Wills et al. [160].

It is very clear from all of this work on hair lipids and age that the lipid levels in hair change with age. Large changes occur both at puberty and around ages 45–55. These changes at middle to advanced age are greater for women than for men. The changes that occur at both of these stages of life involve not only lipid levels, but also composition changes in the hair lipids. Wills et al. [160] in their study on pre- and post-menopausal effects determined that these changes affect hair greasiness, hair shine, hair softness and smoothness. All four of these properties decrease significantly with menopause and age.

In addition to these effects, Mirmirani and Dawson et al. [162] determined that post-menopausal women have significantly lower frontal scalp hair density, lower growth rates and lower hair fiber diameters than pre-menopausal women. A phototrichogram method was used to quantitate these hair parameters. Two studies were conducted by these scientists; an initial study included 44 women, 20 in the post-menopausal group and 24 in the pre-menopausal group. The second study included 177 women (ages 40–60) with 54 in the pre-menopausal, 33 in a

peri-menopausal group (irregular periods or cessation of periods for less than 12 months.) and 90 in the post-menopausal group. Hair growth rate was significantly lower in frontal than occipital regions. Growth rates were also significantly higher in pre-menopausal vs. post-menopausal women in both frontal and occipital sites. Hair density in the occipital site was not affected by menopause; however, hair density in the frontal site was significantly lower in post-menopausal vs. pre-menopausal women.

In both frontal and occipital sites pre-menopausal women had higher anagen percentages than in post-menopausal sites. Average hair fiber diameters were significantly higher in pre-menopausal vs. post-menopausal women in the frontal site, but not in the occipital site (no significant difference). In the expanded study on the frontal site, average fiber diameters were significantly higher in pre-menopausal vs. post-menopausal and peri-menopausal sites. However, there was no significant difference in hair fiber diameters in peri-menopausal and post-menopausal sites. The data suggest that the fiber diameter effect is independent of age. Mirmirami and Dawson et al. concluded that clinical observations support the effects of estrogens on hair biology; however, the current evidence is not adequate to attribute specific hair changes to hormonal effects of menopause.

This decrease in hair fiber diameter with menopause will decrease tensile and bending stiffness of hair fibers. The effects on fiber diameter in combination with the hair density decrease in the frontal region should produce changes in important consumer assessments in that scalp region. For example, hair body will decrease. This effect should appear immediately after shampooing; however the decrease in hair greasiness that will appear after a day or two or longer will tend to partly offset the hair body effect except for the everyday shampooer. I would anticipate related effects on combing ease, that is, as Robbins and Reich [163] have shown the decrease in stiffness will tend to make the hair more difficult to comb while the decrease in hair density/area will tend to make the hair comb easier. Which of these effects are stronger is too difficult to say. Nevertheless, the decrease in hair greasiness will also tend to make the hair more difficult to comb. But, the greasiness effect will take a day or longer after shampooing to take effect. So, the net effects on combing ease are more difficult to predict than on hair body without actual combing data.

2.4.5 The Composition of the Cortex

Since the cortex comprises the major part of the hair fiber mass, results of whole-fiber analysis of hair may be considered to be a good approximation of the composition of the cortex (see Table 2.7). The largest errors resulting from this approximation will be in those amino acids occurring in smaller quantities in the cortex.

Average cortex is rich in cystine (although there is less cystine in cortex than in cuticle). The cortex is also richer in diacidic amino acids and lysine and histidine

than is cuticle. However, the two main components of cortex, the intermediate filaments and the matrix, are very different in chemical composition. The intermediate filament proteins are rich in leucine and in glutamic acid and those amino acids that are generally found in alpha-helical proteins. Although small quantities of cystine (~6%), lysine, and tyrosine are also regularly arranged in the intermediate filaments [143], for additional details see the section entitled, *Type I and II Keratin Proteins* (*IF Proteins*) *of Human Hair* in this Chapter. On the other hand, the matrix is rich in cystine (about 21%, calculated from the sulfur content of gamma keratose of human hair) and proline and those amino acids that resist helix formation such as the KAP Proteins in *The KAP Proteins of Human Hair* in this Chapter. For additional information on the composition of the intermediate filaments and also the matrix, see the section on fractionation and peptide analysis of hair in this Chapter. Also see the section in Chap. 1 entitled *The Origin of Hair Fiber Curvature* which explains the distribution and composition of proteins of different types of cortical cells in human hair.

2.4.6 The Composition of the Medulla

Studies of the medulla of human hair are complicated, because it has poor solubility and is difficult to isolate, see the photomicrographs of the medulla in Chap. 1. In fact, most of the experimental work on medulla has been on African porcupine quill, horse hair, goat hair, or human beard hair medulla rather than medulla of human scalp hair fiber. Rogers [164] described the amino acid composition of medullary protein isolated from porcupine quill, and his results are summarized in Table 2.7 showing very low levels of cysteine and high levels of basic amino acids such as lysine and acidic amino acids such as glutamic acid.

Blackburn [165] determined some of the amino acids from medulla of wool fibers. Most wool fibers do not contain a medulla; however, some coarse wool like kemp or mohair does contain this porous component. Although Blackburn's results are more qualitative, they agree in general with the data of Rogers, suggesting low cystine content compared to whole fiber, and relatively large amounts of acidic and basic amino acids.

Langbein et al. [166] demonstrated 12 hair keratin proteins and 12 epithelial keratins that are potentially expressed in medullary cells of human beard hair medulla. The genes that form these keratins are located on the type I KRT18 gene along with genes located on chromosomes 17 and 12. These scientists also found a few cortical cells in this same beard hair medulla. This cortical cell effect may be exclusive to human beard hairs because this same pattern has not been reported in other highly medullated animal hairs. Langbein et al. concluded that medulla cells are distinct from all other hair follicle cells in keratin expression profile and keratin number.

If one assumes that medullary protein of porcupine quill is representative of medullary protein of human hair, some interesting comparisons can be made of the

three morphological regions of human hair. Among the gross differences is the fact that cuticle has even higher cystine content than whole fiber while medulla has only trace quantities of cystine. Medulla also appears to have relatively small amounts of hydroxy amino acids and relatively large amounts of basic and acidic amino acids compared to the other two morphological components of animal hairs. These facts suggest that medulla will be more susceptible to reactions with acids and alkalis and to ion exchange reactions such as reactions with anionic and cationic surfactants, ionic dyes and metals. But medulla will be less sensitive to reaction with reducing agents. One must also consider that since medulla is located at the core of the fiber, it is protected by both the cuticle and the cortex and by the slow rate of diffusion through these two morphological regions.

2.5 N-Terminal and C-Terminal Amino Acids and SCMK Fractionation

2.5.1 N-Terminal Amino Acids

Kerr and Godin [167], used the dinitrophenylation method of Sanger [168] and identified valine, threonine, glycine, alanine, serine, glutamic acid, and aspartic acid as N-terminal amino acids in human hair. Quantitative data by Leon [61], Speakman [169] and Hahnel [170] for N-terminal amino acids of human hair are summarized in Table 2.19. All of these references identify the same seven amino acids as N-terminal residues in human hair. In addition, there is agreement for the relative quantities of glycine, alanine, serine, glutamic acid, and aspartic acid as N-terminal groups. However, the quantitative data for valine and threonine are in discord. The apparent disagreement of these data may be due to differences in the relative ratios of the different proteins in the different samples caused by

Table 2.19 N-terminal amino acids in human hair (relative ratios)

Amino acids	Micromol/Gm hair	Relative ratios of amino acids	
		Reference [61]	Reference [170]
Valine	4.0	8	4
Threonine	4.0	8	6
Glycine	3.9	8	8
Alanine	1.0	2	2
Serine	1.0	2	2
Glutamic acid	1.0	2	2
Aspartic acid	0.5	1	1
Total	15.4		

either sampling or experimental procedures. Hahnel [170] reported these same seven amino acids as N-terminal residues in calluses, psoriasis scales, nails and hair fiber.

2.5.2 C-Terminal Amino Acids

The C-terminal amino acids in human hair have been identified by Kerr and Godin [167] using the hydrazinolysis method of Niu and Fraenkel-Conrat [171]. These amino acids are threonine, glycine, alanine, serine, glutamic acid, and aspartic acid. Interestingly, all six of these amino acids also serve as N-terminal residues. These same six C-terminal amino acids have been identified by Bradbury as C-terminal residues in wool fiber [172].

2.5.3 Fractionation Procedures

More extensive peptide investigations of keratin fibers generally consist of solubilizing the keratin; separation of the resultant mixture by means of solubility, chromatography, or electrophoresis; and analysis of the resultant fractions. A commonly used method for preparing keratins for sequencing or peptide analysis consists of solubilizing the keratins with strong reducing solutions, usually salts of dithiothreitol or thioglycolic acid [173] or by using enzymes or mixtures or sequential treatments of reducing agents and enzymes [76]. With the S-carboxy methyl keratin procedure, the reduced keratin is reacted with iodoacetic acid, forming the S-carboxy methyl keratin (SCMK) derivatives [174] to enhance the solubility of the proteinaceous matter and to prevent reoxidation of the thiol groups. Radiolabelled iodoacetic acid is often used to tag the fractions and gel electrophoresis to separate the different protein fractions.

$$\text{K-SH} + \text{I-CH}_2\text{-COOH} \longrightarrow \underset{\text{(SCMK)}}{\text{K-S-CH}_2\text{-COOH}}$$

A relatively large amount of effort has gone into the fractionation of wool fiber into its major protein components and the characterization of the resultant fractions. Thus, the mysteries underlying the detailed structures of the major proteins and polypeptides of wool and human hair fibers are gradually being unraveled. The following papers by Bringans et al. [76], Crewther et al. [175, 176], Gillespie [177], Corfield et al. [178], Cole et al. [179], Chaps. 2 and 3 in the book by Fraser et al. [180], Fraser's paper [181], the book by Rogers et al. [182], and the papers by Swift [183] and by Powell and Rogers [184] and Langbein [185] and are leading entries into this work.

2.6 Major Protein Fractions of Hair and Gene Expression

During the past decade, a considerable amount of work has been done on the fractionation and amino acid sequencing of some of the major proteins of human hair. In addition, expression of genes, using in situ hybridization or reverse transcriptase-polymerase chain reaction (RT-PCR) expression by hair follicles or the use of specific protein antibodies or other techniques have been useful in helping to elucidate where and when the follicle genes are expressed.

The phrase major protein is used in the sense of the highest concentration proteins in the fibers or a specific region of the fibers. In this field, the following abbreviations are commonly used to describe the more important protein types under investigation:

KAP, keratin associated proteins [formerly IFAP (intermediate filament associated proteins)]
IF, intermediate filament proteins, now referred to as keratins [1]
HS, high sulfur proteins
UHS, ultra high sulfur proteins
HT, high tyrosine proteins
HGT, high glycine tyrosine proteins

Rogers [1] described the terms keratin and keratin-associated proteins explaining that the term keratin today generally refers to the intermediate filament proteins of the fiber, a clear distinction from the past. On the other hand, many of the KAPs are the high sulfur and ultra high sulfur proteins that commonly occur in the cuticle as well as in the matrix of the cortex.

For one procedure of analysis, Rogers et al. [182] suggested extracting the hair with dithiothreitol in alkali and 8 M urea, labeling with C14 iodoacetic acid at pH 8 and separation by polyacrylamide gel electrophoresis (PAGE) in sodium decyl sulfate solution. This procedure provides a separation into two major fractions for human hair consisting of high sulfur proteins that are from the matrix and classified as KAP proteins and a second fraction of low sulfur proteins that are IF material. A third fraction from wool fibers, but not present in human hair, consists of HGT proteins that are also matrix or KAP proteins. The status of the research concerned with differentiation into cuticle and cortical KAP proteins and the genes that correspond to these various proteins is summarized in the papers by Powell and G.E. Rogers [184] and in the review by G.E. Rogers [1] and in these two excellent reviews by Langbein and M.A. Rogers [185, 186].

2.6.1 The KAP Proteins of Human Hair

The keratin associated proteins include those that form the matrix of the cortex and the high cystine containing proteins of the cuticle. These proteins were discovered

more than three decades ago and some of their sequences are described in this reference by Powell and G.E. Rogers [184]; however the more recent review by M.A. Rogers and Langbein [187] covers the literature over the three decades leading up to 2006 and is extremely helpful to anyone interested in this area of research. Clusters of genes on at least five chromosomes 17q12-21, 21q22.1, 21q23, 11p15.5 and 11q13.4 are involved in the production of more than 80 different KAPs [80, 159].

The paper by Rogers and Langbein et al. [187] contains a helpful diagram that I have modified and used for the schematic of Fig. 2.4. This diagram illustrates several of the important KAP proteins in human hair cuticle and cortex. Rogers and Langbein suggested that the KAP 5, KAP 10, KAP 17.1 and KAP 12 occur in the largest amounts in human hair cuticle whereas the KAP 1, KAP 2, KAP 3, KAP 4, KAP 9, KAP 7, KAP 19.1 and KAP 19.2 occur in the largest amounts in the cortex. Anyone interested in the KAP's of the human hair cuticle and the cortex, their sequences, the domains that these proteins are found in and their genomic expression should read this review paper by Rogers and Langbein [187].

G.E. Rogers further explained that the KAP proteins of the matrix are a large group of perhaps as many as 100 different proteins. Rogers described the order of expression of genes and thus the synthesis of many of the proteins of the different parts of the hair fiber. The Ultra high sulfur proteins including those of the cuticle are among the last KAP's that are expressed. There are at least two unique families of proteins the KAP5 and KAP10s of the hair cuticle which are major components

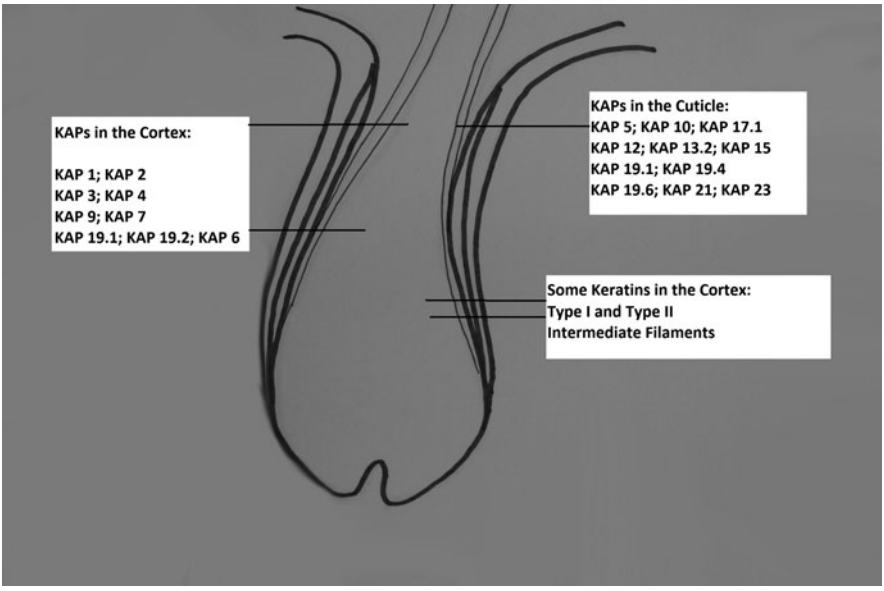


Fig. 2.4 Schematic indicating some KAP proteins of human hair cuticle and cortex, patterned after a schematic by Rogers and Langbein [159]

of the exocuticle [1], the A-layer [76] and the epicuticle membrane of the hair surface and of cuticle cells [95].

The HS proteins generally contain about 20% of their residues as half-cystine and the UHS proteins usually contain between 30% and 35% residues of half-cystine. These latter proteins in wool have been shown to be affected by the cystine/cysteine level in the wool follicle [1] which is determined by the cystine/cysteine level in the plasma. Proline generally occurs in the high sulfur proteins at a relatively high level (about 7–9%) and has been suggested as an indicator for the HS proteins. Marshall and Gillespie [29] suggested that the half cystine content of normal human scalp hair should be in the range of 17–18% and should not vary with age, but should vary only from sunlight, cosmetic treatment and biochemical abnormalities.

Although, the HS and UHS proteins are rich in half-cystine they contain very little to no methionine. Methionine, in the diet, is important to these proteins because it can be converted into cysteine [184]. The important role of cystine/cysteine in protein synthesis and to hair growth in the follicle is summarized well by Powell and Rogers [184] who described this subject in great detail. In the late 1990s there were at least eight families of KAP's ranging from 12 to 41 mol% cystine. As indicated before, there are also glycine-tyrosine rich KAP's, high sulfur cuticle KAP's and high sulfur cortex KAP's among others.

Jenkins and Powell [188] examined five proteins expressed by the KAP5 family of genes in sheep that encodes cysteine rich/glycine rich keratins in the cuticle. All of these proteins are high cysteine (~30%), high glycine (~27%) proteins of the cuticle and in humans this gene family (KAP5) is from chromosome 11. Rogers in his lucid review paper described this complex area even detailing some of the signals that regulate cell specificity and gene expression. For further details of this area of research see the excellent reviews by Professor George Rogers [1] and the outstanding reviews by M.A. Rogers and Langbein [185–187].

2.6.2 Type I and II Keratin Proteins (IF Proteins) of Human Hair

Two of the six different Types of IF Proteins are found in human hair. Type I and Type II keratins are distinguished by their isoelectric point, the Type I proteins being acidic and the Type II being basic or neutral. The nomenclature for the hair keratins is explained in Chap. 1 in Table 1.16. Important references on these important proteins are [185–189]. Langbein and M.A. Rogers et al. [185, 186] and Langbein and Schweitzer [189] described that the human hair keratin gene families have nine members in the Type I family and six members in the Type II family. The genes are on human chromosomes 17q12-21 and 12q13 and there are 15 functional genes, 9 for the Type I and 6 for the Type II families. The highest expressed keratins of the cuticle are: Type I hHa5 (K35) and hHa2 (K32) and for

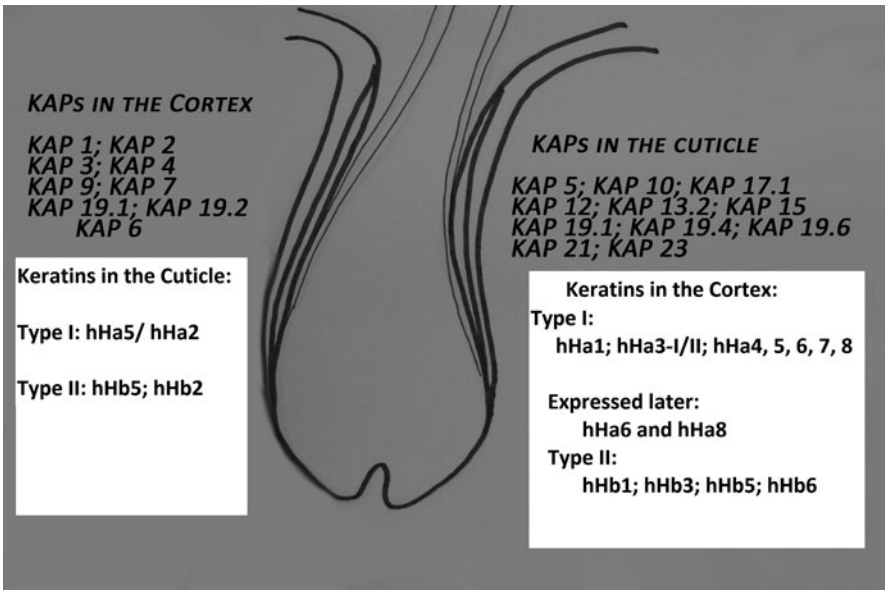


Fig. 2.5 Schematic summarizing the IF keratins of human hair; Data from Rogers and Langbein [157, 158]

Type II are hHb5 (K85) and hHb2 (K82). Three of these same keratins are also in the matrix of the cortex: hHa5 (K35), hHa2 (K32) and hHb5 (K85). The Type I keratins of the middle to upper cortex are hHa1 (K31), hHa3-I (K33a)/II (K33b), hHa4 (K34), hHa5 (K35), hHa6 (K36), hHa7 (K37) and hHa8 (K38). Type II keratins of cortex are hHb1 (K81), hHb3 (K83), hHb5 (K85) and hHb6 (K86) [185, 186] see Fig. 2.5. The names in parenthesis are a newer nomenclature.

The intermediate filaments in different tissues show some similarity in form; see Fig. 1.36 in Chap. 1 in the section entitled *Intermediate Filaments* for a discussion of these structures; however these structures differ considerably in their exact composition and configuration [186–189]. The common structural feature among this class of proteins is the central helical rod [188]. On the other hand, a primary difference is in the amino and carboxyl domains. These domains vary in both amino acid sequences and size [189]. The end domains contain many cysteine residues and these can even form cystine cross-links with cysteine residues of KAP proteins of the matrix.

As described above, the intermediate filament protein molecules in keratins are composed of two different types of polypeptides, Type I (acidic side chains) and Type II (neutral to basic side chains). Equimolar quantities of a Type I and Type II are necessary to form an Intermediate filament (Fig. 1.36). These two chains initially coil about each other forming a two strand coiled-coil rope, thus the initial formation of each filament requires one acidic polypeptide that coils about a basic

polypeptide partner or mate. Additional coiled coils join together end to end and laterally. For additional details and references see Chap. 1 in the section entitled *Intermediate Filaments*.

The cystine content of the low sulfur intermediate filament regions is about 6% and is not uniformly dispersed between domains of an intermediate filament chain. The rod domain contains about only 3% half-cystine or as little as one half-cystine residue, while the N terminal domain contains about 11% half-cystine and the C terminal unit about 17% half-cystine [190, 191]. It would appear that these half-cystine residues are involved in disulfide linkages but that many more disulfide residues exist in the matrix.

The acidic Type I intermediate filament proteins of human hair represent a class of proteins that are about 44 and 46 K in molecular weight, while the basic-neutral Type II proteins are about 50, 59, and 60 K [192]. Langbein and Schweitzer [189] described the IFs of the Medulla, the inner root sheath, the outer root sheath and the companion layer and discussed even newer nomenclatures for this important class of hair proteins. Amino acid sequences for the intermediate filament polypeptides from several proteins including wool fiber were initially described by Crewther et al. [176]. For a more comprehensive discussion of the IFs, see the manuscript by Powell and Rogers [184] and the references therein; also see the more recent reviews by Rogers [1] and the important papers by Langbein and M.A. Rogers and especially the review by Langbein and Schweitzer [189] and the discussion and references in Chap. 1 in the section entitled *Intermediate Filaments*. Intermediate filaments are involved in a large number of diseases. For a lead into that subject see Chap. 3 and the discussion on *Hair Abnormalities*.

2.6.3 Tricohyalin Protein

Tricohyalin is a granular, proteinaceous material found in the cytoplasm of cells of the inner root sheath that envelopes the growing hair fiber; see Fig. 1.6 of Chap. 1. It is a major protein synthesized during hair growth and can also be found in the matrix of the cortex and in the medulla of fully formed hair fibers. However, its role in the growth of human hair fibers is not fully understood at this time. The amino acid composition of tricohyalin protein found in sheep, guinea pig and human hair follicles has been reported by Rogers et al. [193]. Tricohyalin contains citrulline resulting from arginine conversion through the enzyme peptidyl arginine deiminase [192]. It also contains many repeat units and is larger in human hair than in wool fiber (1,897 vs. 1,549 amino acid residues). Its sequencing studies show that tricohyalin is not a precursor of IF proteins. For more details on this unique protein, see the review by Powell and Rogers [184].

2.7 Other Protein Fractionation Methods

An older method of fractionation of keratin fibers, the method of Alexander and Earland [97, 194, 195], consists of oxidation of the disulfide bonds of the hair to sulfonic acid groups, using aqueous peracetic acid solution, and separation of the oxidized proteins, generally by differences in solubilities of the different components of the mixture. The primary three fractions in this separation are called keratoses. The amino acid composition of these three fractions isolated from merino wool has been reported by Corfield et al. [195].

Fractionation of human hair into keratoses by the method of Alexander and Earland [97] as modified by Corfield et al. [195] has been reported for human hair by Menkart et al. [25] (see Table 2.20). This procedure consists of oxidation of the fibers with aqueous peracetic acid and solubilization in dilute alkali. The insoluble fraction is called beta keratose and is believed to consist of proteins derived primarily from cell membranes and similar matter. See the previous section in this Chapter entitled, *Proteins in the Cortical Cell Membranes*, describing an amino acid analysis of an extract of this fraction. Acidification of the solution to pH 4.0 produces a precipitate called alpha keratose that is believed to originate primarily in the crystalline or fibrillar regions of the cortex. The material remaining in solution has been labeled gamma keratose. It is the fraction containing the largest percentage of sulfur (see Table 2.20) and is believed to consist of proteins derived primarily from the amorphous regions of the fibers (primarily from the matrix of the cortex). Of special interest is the significantly larger gamma keratose fraction from human hair compared to merino wool (see Table 2.20). This is consistent with the higher cystine content in human hair.

Using a similar procedure, Crounse [196] examined a portion of the alpha keratose fraction by quantitative amino acid analysis. He found similar quantities in the amino acids of this fraction obtained from human hair and from fractions of nails and epidermis, except for cystine, cysteine, and glycine.

A modified version of this procedure has been described by Wolfram and Milligan [197]. Their procedure involves esterification of the carboxyl groups that are believed to reside primarily on the alpha-helical proteins and proteins of the hair surface. Esterification decreases the solubility of these proteins, allowing the non-esterified proteins (of the matrix) to be extracted more easily. The soluble fraction of this procedure is called gamma*keratose; it resembles gamma keratose but provides a higher yield. The insoluble residue exhibits birefringence and is called the alpha-beta*keratose fraction.

Table 2.20 Percent keratoses in human hair [25]

Fiber type	Alpha-keratose	Beta-keratose	Gamma-keratose	Total
Merino wool	56 (1.88)[a]	10 (2.13)	25 (5.84)	91
Caucasian hair	43 (2.38)	14 (4.00)	33 (6.60)	90

[a]Percent sulfur in parentheses [25]

Other fractionations of human hair have been reported by Vickery et al. [26] and Andrews and deBeer [135] and by Lustig et al. [136]. The former paper describes a hydrolytic separation and the latter a fractionation by sulfonation followed by reduction [19]. These procedures have not been pursued to a great extent because of the inherent amino acid degradation in the initial solubilization reaction.

2.8 Diet and Hair Composition

Ultra high sulfur protein production appears to be very sensitive to the amount of cysteine that is present in the diet of sheep [198] or available in the follicle. The same phenomenon most likely exists for human hair. Other than malnutrition, hair proteins have not been shown to be influenced by diet. Campbell et al. [198] demonstrated via nutritional studies on sheep that crimp frequency can be explained by considering fiber growth rates as influenced by diet; see the data of Table 2.21. These data show that crimp counts increase at low nutritional levels where the growth rates are slower for both high crimp and low crimp producing sheep. The percentages of sulfur and of high sulfur proteins also decrease at the low nutritional levels where growth rates are slower. So protein composition as influenced by diet (malnutrition vs. normal nutrition) affects the ratio of high to low sulfur proteins in sheep and it plays a role in determining hair fiber curvature. It is likely that this same effect exists in humans, because of the results described (below) on malnutrition effects on hair composition and growth.

Studies of the effects of diet in persons suffering malnutrition such as protein deficiencies show that diet supplementation can influence the protein composition of human hair. However, such effects have only been demonstrated among persons suffering from severe malnutrition and never among healthy persons on a normal diet. For example, the cystine, arginine, and methionine contents of human hair have been reported to be influenced by diet that is insufficient in protein content. Koyanagi and Takanohashi [142] conducted a study among eight- to nine-year-old Japanese children who had been fed millet and very little animal protein. Analysis of the hair from these children revealed cystine contents as low as 8.1% (675 μmol half cystine per gram of hair) rather than 17–18% as suggested by Marshall [29] as the normal half cystine level in humans. Diet supplementation with shark liver oil produced a significant increase in the cystine content of the hair among these children. Diet supplementation with skim milk for 6 months produced an even larger increase in cysteine, most likely from an increased synthesis of the Ultra high sulfur proteins.

Table 2.21 Effect of nutrition on high S Proteins & Crimp from Campbell et al. [198]

Nutritional level	High crimp wool			Low crimp wool		
	Norm	Low	Norm	Norm	Low	Norm
Crimps/cm	7.0	9.0	6.7	1.7	3.8	2.0
% S	4.08	3.17	4.08	3.26	2.75	3.22
% High S Prot.	32	22	29	24	17	20

Although, the HS and UHS proteins are rich in half-cystine they contain virtually no methionine. Methionine in the diet is important to these proteins because it can be converted into cysteine and cystine [184]. The important role of cystine/cysteine in protein synthesis and to hair growth in the follicle is summarized well by Powell and Rogers [184].

Cystine, methionine, and sulfur contents of the hair of children suffering from kwashiorkor have also been reported to be lower than that of normal children [199]. The arginine content of hair has been reported to decrease as a result of kwashiorkor [200]. In fact, Noer and Garrigues [200] reported arginine contents of human hair in severe cases of kwashiorkor, as low as one-half the normal level. By analogy with the effects of diet and sulfur enrichment on the high-sulfur proteins in wool fiber [201, 202], these effects of a lower arginine content in hair are probably a result of a decreased synthesis of the sulfur-rich proteins that likely contain arginine too.

Cosmetic advertisements abound with the suggested or implied nutrient or health-benefit claims provided by proteins or vitamins or even provitamins in cosmetic products. Marshall and Gillespie [202] offer the following conclusion with regard to nutrition and hair. "In healthy humans, it is unlikely that any significant variation in the proteins of hair will result from normal changes in nutrition." Therefore, it is much less likely that such changes could ever be induced from these same ingredients or their precursors when applied topically in a shampoo or a hair conditioner.

In fact, there have been no systematic studies of the effects of nutrients like vitamins on the rate of wool or hair growth or structure. However, there are some indications that in dietary insufficiencies, supplements of folic acid (a B complex vitamin) or pyridoxine (a B complex vitamin, B6) could be helpful to hair growth. The logic behind these indications is that these vitamins play a role in cysteine metabolism. However, cysteine metabolism does not take place in the non-living part of the hair fiber. On the other hand, panthenol, the precursor to pantothenic acid (another B complex vitamin) has never been demonstrated in any published scientific study to affect the nutrition or growth of hair. In a review on nutrition and hair, Flesch [148] reported, "There is no objective evidence available to support the assumption that pantothenic acid has a biochemical role in the production of hair." Thus, there is no current objective evidence to support a nutritional benefit to hair by this vitamin precursor.

Among sheep with dietary insufficiencies, the minerals copper and zinc when supplemented to the diet have been shown to be important to wool fiber growth. Their effectiveness is attributed to the important roles these minerals play in sulfur amino acid metabolism; copper serves to catalyze the oxidation of cysteine to cystine cross-links during fiber synthesis [203]. A related effect has been shown to occur in African children with a deficiency in riboflavin and pantothenic acid wherein the hair grows with no or minimal pigment and is straight. This effect has been associated with a copper deficiency and is explained in Chap. 3. Zinc is required for cell division to occur and it also appears to play a role in liver disease and protein metabolism [204].

2.9 The Analysis and Origin of Protein Fragments from Damaged Hair: Useful Methodology for the Future

Partial removal and analysis of proteinaceous matter from damaged keratin fibers can be traced back to the alkali solubility test. The alkali solubility test involves exposing a weighed amount of hair to a fixed volume of 0.1 N sodium hydroxide solution at 20°C for a fixed time [205, 206] and isolating, drying and weighing the hair. The loss in weight provides the amount of protein loss from the keratin which is almost always greater in damaged hair than undamaged hair. For example, Dubief [40] examined undamaged hair, the same hair exposed to visible light and hair exposed to UV plus visible light and found 1%, 1.6% and 3.5% alkaline soluble matter respectively. Inglis and Leaver [45] were one of the first to show that proteinaceous derived fragments were removed or dissolved into the bleach bath by treatment of wool fiber with aqueous alkaline hydrogen peroxide treatment.

Various schemes to solubilize and isolate the proteinaceous fragments or matter from damaged hair have subsequently been tried. Oku et al. [207] analyzed total proteinaceous fragments from the hair dissolved in permanent wave solutions and recommended this as an assay for hair damage. Sandhu and Robbins [208] shook chemically damaged and control hair fibers in water or detergent solutions and analyzed the total dissolved and insoluble proteinaceous matter separately and together by the Lowry test. Inoue, Ito and Kizawa [209] extracted the hair with different reducing solutions and analyzed the extracted proteinaceous matter which they called Labile proteins by the BioRad Protein assay. The amount of extracted proteinaceous matter from the hair of three different permed treatments by these scientists appeared to relate to the reduction in the tensile breaking force. Ruetsch, Yang and Kamath [210] extracted bleached hair, UV treated hair, permed hair and bleached/UV treated hair and bleached/permed hair with 0.05 M dithiothreitol, 8 M urea and Tris buffer for 24 h and then sonicated the extract for 30 min. They then derivatized the reduced hair with 20% iodoacetamide to prevent reoxidation. These extracts were then separated and analyzed by electrophoresis. Some of the conclusions from this study were:

- Chemical bleaching with alkaline peroxide, fragments the matrix and the intermediate filament proteins,
- Permanent waving hair produces soluble fragments from the matrix proteins,
- Multiple perms and permanent waving followed by UV treatment decreases the Intermediate filament extractable protein fragments, but the matrix protein fragments can still be extracted. Multiple perming and UV treatment can render IF proteins less extractable possibly by producing higher molecular weight proteins via cross-linking or fusion reactions see Chap. 5 in the section entitled *Long Term Irradiation Produces Fusion Reactions Across Structural Boundaries*. Shorter term UV treatments were not examined.

More recently Sinclair, Davis and Flagler et al. [211] analyzed water solutions and suspensions from shaking hairs in water similar to the method of Sandhu and Robbins, but Davis and Flagler took this method to a higher level by determining some of the hair proteins from which the fragments/matter were actually derived. Davis and Flagler [211, Davis MG, Flagler M. Private communication] analyzed the proteinaceous matter in solutions and suspensions from bleached and undamaged hair via Matrix assisted laser desorption ionization-Time of flight mass spectrometry (MALDI-TOF) and also by 2 Dimensional Gel Electrophoresis (2DGE) and demonstrated significant decreases in chemically bleached hair in these cortex proteins: acidic keratins 31, 33a, 33b and basic keratins 81, 83, 85 and 86. K32 of the cuticle was also decreased by bleaching. This assay currently is not as amenable to KAP proteins as it is to keratins which may be due to the small fragment size requirements for mass spec analysis. More creative extension to this type of procedure should expand its utility and reveal very useful information in the future for hair research.

2.10 Water: A Fundamental Component of Human Hair

Table 2.22 summarizes the effects of relative humidity on the water content of human hair (Anzuino G. Private communication). Additional data are described in Chap. 9 in the section entitled *Water (RH), pH and Solvents and the Dimensions of Hair*. Obviously, the determined moisture content of keratin fibers depends on the conditions selected as the state of dryness [142] as well as on the RH. The amount of moisture in hair also plays a critical role in its physical and cosmetic properties, as described in Chap. 9. The data of Table 2.22 were obtained by dehydration of the fibers in a dry box over calcium chloride and determining the regain at increasing humidity. Chamberlain and Speakman [212] reported the moisture content of human hair by moisture regain from the dry state and by way of dehydration from 100% RH. Their data show a hysteresis wherein the moisture contents at intermediate humidity are slightly lower by the hydration method than by dehydration. This hysteresis phenomenon is described in more detail in Chap. 9.

Similarly, hair dried with heat can exhibit lower moisture content than hair dried at room temperature [213]. After heat-drying, hair absorbs moisture but does not

Table 2.22 Water content of hair at different relative humidities

RH[a]	Approximate moisture content[b] (%)
29.2	6.0
40.3	7.6
50.0	9.8
65.0	12.8
70.3	13.6

[a]Temperature = 74°F

[b]Each value is an average of five determinations on dark brown Italian hair from DeMeo Bros. reported to be undamaged chemically. The hair was not extracted with solvent

return to the room temperature dried moisture level until it is either rewet with water or conditioned at a higher relative humidity. Thus, a hysteresis exists between heat-dried hair and room temperature dried-hair similar to that from absorption vs. desorption of moisture.

Hysteresis phenomena in the water sorption by high polymers [214] and by other proteins such as wool fiber [215] and casein [216] have also been described. Smith [214] suggested that hysteresis is a result of differences in the ratio of "bound" to "free" water in the substrate, with a larger amount of bound water present on desorption than on absorption because more water binding sites are accessible from the wet state than the dry state.

Undoubtedly, the several hydrophilic side chains (guanidino, amino, carboxyl, hydroxyl, phenolic, etc.) and peptide bonds of keratin fibers contribute to water sorption, although there is controversy over the primary water-binding groups. Leeder and Watt [216], in a very interesting study involving water sorption of unaltered and deaminated wool fibers, concluded that the binding of water by amino and guanidino groups is responsible for a large percentage of the water sorption capacity of keratin fibers, especially at low humidities. On the other hand, Breuer concluded that the peptide bonds are preferential sites for hydration [60].

The conclusions of Leeder and Watt are supported by Pauling [217], who described the negligible attraction of water by the polypeptide nylon, and the apparent agreement between the number of molecules of water initially sorbed by several proteins and the number of polar side-chain groups in those proteins.

Spectroscopic studies of the nuclear magnetic resonance (NMR) of both human hair [218] and wool fiber [219] indicated that the protons of water in keratin fibers are hydrogen-bonded and are less mobile than in the bulk liquid. At relative humidity, below 25%, water molecules are principally bonded to hydrophilic sites of the fiber by hydrogen bonds and can be described by Langmuir's fundamental theory for the absorption of gases on solids [220]. As the humidity increases, additional water is sorbed, producing a decrease in the energy of binding of water already associated with the protein. At very high RH, above 80%, multi-molecular sorption (water on water) becomes increasingly important.

Feughelman and Haly [220] and Cassie [221] suggested two different models for estimating the amounts of bound "un-mobile" and mobile "free or liquid" water present in keratin fibers. Feughelman and Haly defined bound water as water associated with the keratin structure and mobile water as water not associated directly with the keratin structure. This model considers the decrease in energy of binding of water molecules already associated with the keratin structure with increasing water content. King [222] discusses two- and three-phase adsorption theories to explain the adsorption of moisture by textile materials. His conclusions and cautions are pertinent to this same phenomenon in human hair. King suggested that it is relatively easy to derive a sorption isotherm that fits an empirical relation using two or three adjustable coefficients, and he cautioned others in keratin science to make sure the theory they consider does not contradict accepted physical principles. The effects of water on swelling, friction, tensile, and other properties of human hair are described in Chap. 9.

2.11 Trace Metals in Human Hair

There are a number of studies describing the quantitative determination of various elements of human hair other than carbon, hydrogen, nitrogen, oxygen, and sulfur. In particular, the inorganic constituents of human hair appear to be receiving some attention because of their potential in diagnostic medicine as described by Maugh [223], and to a lesser degree in forensic science. However, the fact that certain transition metals such as iron and copper can catalyze the formation of free radicals in oxidative reactions has picked up interest in cosmetic science too.

The mineral content of human hair fibers is generally very low (less than 1%). It is sometimes difficult to determine whether this inorganic matter is derived from an extraneous source (which much of it is) or whether it arises during fiber synthesis. In addition, many metals of human hair exist as an integral part of the fiber structure, such as salt linkages or coordination complexes with the side chains of the proteins or pigments, although the possibility of mineral deposits or compound deposits as in soap deposition also exists.

Pautard [224] reported the total ash content of human hair to be as low as 0.26% of the dry weight of the fibers. But, Dutcher and Rothman [225] reported ash contents to vary from 0.55% to 0.94%. Among the trace elements reported in human hair are Ca, Mg, Sr, B, Al, Na, K, Zn, Cu, Mn, Fe, Ag, Au, Hg, As, Pb, Sb, Ti, W, V, Mo, I, P, and Se. The actual origin of most of these elements in human hair is due to a variety of sources that are described below. However, from a study involving quantitative analysis of 13 elements in human hair and in hair wash solutions, Bate et al. [226] concluded that a large portion of the trace elements in the hair originate from sweat deposits.

In the case of metals, the water supply generally provides calcium and magnesium to hair. Smart et al. [227] reported that oxidation dyed hair washed multiple times in tap water accumulates high concentrations of metals in the sulfonate rich exocuticle of the hair. This nano-scale ion mass spectrometric study provides evidence that calcium binds to the sulfonate groups produced by oxidation. Common transition metals such as iron, manganese and copper also deposit in hair from the water supply. Copper from swimming pools has been reported by Bhat et al. [228] to turn blond hair green at low concentrations. Other sources of metals in hair are sweat deposits, diet, air pollution, and metabolic irregularities. Metal contamination can also arise from hair products that provide zinc or selenium (antidandruff products), potassium, sodium, or magnesium (soaps or shampoos), and even lead from lead acetate-containing hair dyes.

2.11.1 Transition Metals and Free Radical Reactions

The Transition metals Fe, Cu, Mn, Co and V are very active and can participate in one electron transfer reactions and thereby participate in free radical reactions.

Of these metals, Fe and Cu are the most likely to be found in human hair and will be the focus of this discussion. As described in Chap. 5, trace quantities of these metals can participate with either hydrogen peroxide or hydroperoxides formed in hair to form hydroxyl radicals through the Fenton reaction. In addition, free radicals can be formed by direct photolysis of hydroperoxides. Some iron complexes or phenolics [229] or even the excitation of dyes or fluorescent whitening agents in the presence of one electron donors (Fe, Cu, Mn, Co and V) as described by Millington [230] can produce superoxide radical by a variety of reactions including autoxidation of mercaptans such as cysteine. Transition metals in hair can be endogenous or exogenous. Exogenous sources are:

– The water supply used for bathing and washing hair
– Swimming pool water
– Airborne pollutants

Kempson et al. [231] cited a study by Trunova et al. [232] who concluded that Cu and a few other elements are reliable indicators of endogenous consumption, but Fe and Ca are not. This citation suggests that Fe and Ca contents of hair are more readily affected by environmental influences than Cu. Cu is involved in two important metabolic processes; one in the keratinization of human hair fibers (oxidation of thiol to disulfide) and in the oxidation of tyrosine to melanin involving the enzyme tyrosinase which also requires Cu [233]. Therefore, Cu is endogenous [234] to hair fibers. However, Cu can also arise in hair from exogenous sources such as swimming pool water producing the green hair phenomenon [228]. Ca is primarily exogenous in origin. Although Fe and Cu are also exogenous metals, the study by Trunova et al. (above) suggested that the Fe content of hair is influenced more by exogenous sources than the Cu content of hair [232, 233]. As indicated earlier, this study by Trunova suggested that Ca and Fe will compete more effectively (not exclusively) than Cu for acidic sites on hair including sulfonate and carboxylic acid sites.

2.11.2 Functional Groups that Bind Specific Metals

Kempson et al. [231] reviewed the existence in human hair for metals like Cu and Zn with some data on Fe and Ca and other metals. They suggested that Ca has a higher affinity for carboxylic acid and sulfonate groups than Cu. These same scientists suggested that Cu(II) has a preference for binding with primary amine groups $\{-NH_2\}$ and Cu(I) has a higher affinity for thiol groups $\{-SH\}$. Kempson et al. also stated that "perhaps. . .Cu and Zn do not form soaps with lipids" in hair, however, Cu is known to form water insoluble soaps in-vitro when reacted with lipids such as butter or with oils such as cottonseed oil or soy bean oil as described by Berry [235]. It may be that Ca has a higher affinity for carboxylic acids and sulfonic acids in hair, but Cu does actually react to form "soaps" with carboxylic acids, but perhaps to a lesser degree in the presence of Ca.

2.11.3 Regions of the Fiber that have a High Affinity for Metals

Regions of high carboxylic acid content are the endocuticle, the cell membrane complex (especially the CMC of the cortex) and the medulla. These areas of the fiber are likely to have a high affinity for divalent and trivalent metals. Therefore, these areas are likely to absorb Ca and Fe with smaller amounts of Cu if the metals can diffuse to those regions. In the case of oxidation dyed or bleached hair the high cystine containing regions of the fibers (A-layer, exocuticle, cuticle cell membranes, and the matrix of the cortex) will also contain large amounts of sulfonate and will attract Ca and Fe and also Cu. Calcium has been shown by Smart et al. [227] to accumulate in the sulfonate rich exocuticle of oxidation dyed hair.

2.11.3.1 Pigments of Hair Contain High Metal Content

The pigments of human hair are described as containing more metals than other regions of the fibers. Dutcher and Rothman [225] reported that the iron content in red hair is higher than in hair of other colors, while Kosla et al. [236] in Warsaw Poland found that hair of schnauzer dogs contains more Fe than hair of humans, but found no effect of color. Furthermore, Liu et al. [237] determined that significant amounts of Cu and Zn are bound to both black-hair and red-hair melanosomes, however, the Fe content is four times higher in red-hair melanosomes. The pigments of human hair are also capable of producing hydroxyl and other free radicals as shown by Qu et al. [238] and also by Haywood [239].

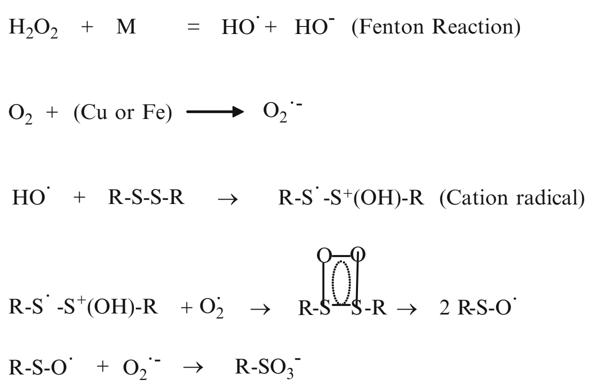
2.11.4 Simulated Swimming Pool and Copper Binding to Hair

Rhamachandran Bhat et al. [228] in an attempt to simulate Cu sorption from swimming pool water containing copper based algaecide concluded that natural white or lightly bleached blonde hair will absorb Cu from 10 ppm Cu solution as $CuSO_4 \cdot 5H_2O$ at pH 5.9 in chlorox containing water after 1 h. Bleached hair absorbed more Cu than non-bleached hair, the non-bleached hair turned light green and the bleached hair darker green. In both cases the absorbed Cu was in the periphery of the hair as shown by EDXA-SEM cross-sections. Interestingly, pre-treatment of the hair with a quaternary ammonium conditioner inhibited the color formation in the hair, probably by competitive inhibition. Nevertheless, small amounts of Cu were still found in the hair with about three times the amount in the lightly bleached hair.

2.11.5 Metals that Bind to Hair do so Specifically

As indicated above, metals like Cu and Fe can bind to polar groups in hair to participate in oxidation-reduction reactions by generating active oxygen compounds such as in the Fenton or other reactions. They can also bind to groups in hair such as sulfur groups and participate in electron transfer from the metal to sulfur or the reverse. For example, Maletin et al. [240] studied the mechanism of the oxidation of copper(I) ions with thiuram disulfide and determined that the rate of the reaction occurred by one electron transfer from the Cu + ion to the disulfide in a complex of this type $[Cu^{I}(\text{disulfide})]^{+}$ to form the anion radical of the disulfide complex. This anion radical then dissociated leading to the formation of a Cu++ adduct of the dithiocarbamate. Simpler disulfides (simpler than thiuram disulfide) will form a complex of the $[Cu^{I}(\text{disulfide})]^{+}$ type and then by one electron transfer will form the anion radical of the disulfide complex (or cation radical of the disulfide) which will then dissociate to form the thiyl radical and thiolate anion or the sulfinyl radical (in the case of the cation radical). The thiyl radical or radical ions produced will participate in oxidation reactions as described in this paper to form cysteic acid or other products. Thiuram disulfide was selected for this study because of its specific spectroscopic properties.

2.11.6 A Proposal for Free Radical Oxidation of Disulfide in Hair by Alkaline Peroxide



The disulfide cation radical is involved in this reaction scheme because it involves oxidation by superoxide anion radical for which some evidence has been provided in the oxidation of cystine and another disulfide with hydrogen peroxide in aqueous solution by Katritzky et al. [241]. Misra [229] determined that superoxide

can be generated by the autoxidation of a large number of compounds including thiols [229], some iron complexes [229] and quinines [229]. Millington determined that some dyes [230] are capable of generating this reactive oxygen species. In addition, Bruskov et al. [242] generated superoxide anion radical by heating (40°C) aqueous buffers saturated with air containing transition metal ion impurities (copper and iron) which serve as electron donors. Molecular oxygen could also oxidize the sulfinyl radical to cysteic acid. Other free radical mechanisms along with more details on oxidation of the disulfide and thioester bonds in hair are described in Chap. 5 in the section entitled *Mechanisms for Free Radical Reactions in Human Hair*. If this scheme is involved in the oxidation of keratin by alkaline peroxide it could explain why alkaline peroxide is more damaging than peroxycarbonate.

2.11.7 Heavy (Toxic) Metals in Human Hair

Although heavy metals occur at low concentrations in human hair, they sometimes accumulate at concentrations well above those levels present in blood or urine. Concentrations of metals such as cadmium, arsenic, mercury, and lead in hair tend to correlate with the amounts of these same metals in internal organs [223]. This is one of the reasons why hair is being considered as a diagnostic tool. Wesenberg et al. [243] found a positive correlation between cadmium levels of hair and target organs (femur, kidney, liver, spleen, heart, muscle tissue, and adrenal glands of Wister rats). Fowler [244] indicated that the highest levels of arsenic in humans are normally found in hair, nails, and skin. Furthermore, it is well known that human hair serves as a tissue for the localization of arsenic during arsenic poisoning.

Hasan et al. [245] reported significantly higher levels of nickel, arsenic, cadmium and mercury in the hair of children living in urban vs. rural areas of the United Arab Emirates. Conclusions were that heavy metal contamination could be due to industrial activity and that hair analysis has the potential of being an effective tool for evaluating toxic elements in humans. Heavy metals such as lead can also arise from air pollution. For example, Milosevic et al. [246] showed significantly higher concentrations of lead in hair of 200 persons living within 5 km of a lead smelter plant than in a control group of 200 persons living at a distance more than 10 km from that same pollution source.

2.11.8 Other Disorders Related to Accumulation of Metals in Human Hair

Analysis of hair can often serve as an indication of even more complicated disorders. For example, a study by Capel et al. [247] indicated significantly higher concentrations of cadmium in hair from dyslexic children than in a normal control group. These scientists suggested that cadmium analysis of hair may be used in

early detection and that excessive cadmium may be involved in this type of learning disorder.

Dankes [248] described Menkes syndrome as being linked to a copper deficiency resulting in abnormal keratinization because copper is involved in the oxidation of cysteine to cystine during keratinization. In this genetic disorder, kinky hair is symptomatic of this disease. This kinky hair results from an unusually high mercaptan level of cysteine, wherein only about 50% of the cysteine is oxidized to disulfide bonds during keratinization.

Children with cystic fibrosis have been found to contain several times the normal level of sodium in their hair and considerably less than normal calcium [223]. Persons suffering from phenylketonuria (phenyl ketones in the urine) contain less than average concentrations of calcium and magnesium in their hair [223]. Victims of kwashiorkor have higher than normal levels of zinc in their hair [223] and low levels of sulfur and the cystine rich proteins [171]. Hair analysis has also been considered as a screening tool for diabetes, because low levels of chromium in the hair have been demonstrated in victims of juvenile-onset diabetes [223]. Hair analysis offers possibilities for diagnosis of several other maladies or disabilities. For more information on this subject see the review by Maugh [223] and the book edited by Brown and Crounse [249].

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Chapter 3
Genetic Control/Involvement in Hair Fiber Traits

Abstract The focus in this chapter is on hair form or fiber diameter and curvature and on hair color or pigmentation. These important hair characteristics are controlled by single nucleotide polymorphisms which are single nucleotide changes in genes. The three primary hair forms today (African, Asian and Caucasian) and their hair pigmentations arose from genetic mutations that are consistent with geographic migrations of Asians and Caucasians. Therefore, these hair forms and pigmentations are probably remnants of prior adaptations to temperature, sun exposure and other environmental influences. Other hair traits related to genetics including different alopecia and several genetically involved hair abnormalities are described along with a brief summary of current directions in forensic science which has expanded into DNA analysis and is moving into the analysis of SNPs.

3.1 Introduction

Traits or characteristics of human hair fibers under genetic control include different hair forms or shapes such as curvature, ellipticity and coarseness, hair colors or pigmentation, and types of baldness, and hair diseases including certain genetically related hair abnormalities. In addition, Heywood et al. [1] suggested evidence for genetic involvement in hair quality. These areas are the subject of the following sections of this chapter. However, the focus of this chapter is on hair form and hair color or pigmentation with regard to single nucleotide polymorphisms (SNPs) which are single nucleotide changes in a gene. Several genetically involved hair abnormalities are also included in this chapter as well as a brief summary of the current direction in forensic science which over the last two decades has expanded dramatically into DNA analysis and is currently moving into the analysis of SNPs. Chapter 2, in the section entitled *Major Protein Fractions of Hair and Gene Expression*, contains a summary of the chromosomes and genes for the important Intermediate Filament proteins (keratin proteins) and KAP (keratin associated proteins) proteins of human hair.

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The term race applies to sub-populations or groups of people similar in several biological characteristics. In the past, races developed and persisted because travel over large distances was limited, thus, similar peoples interacted and procreated. The geographic or racial differences that are found today in hair and skin type are most likely remnants of prior adaptations to temperature, sun exposure and other environmental influences.

The words ethnic and ethnicity have been misused in the cosmetic industry. Ethnicity relates more to similarities in or shared social customs. Race relates more to similarities in physical characteristics. In the following pages I refer to geo-racial or geo-ethnic groups linking geographic origin to race or ethnicity. I will try to refrain from using the phrase ethnic hair, but I will sometimes inadvertently use the term geo-ethnic group. The cosmetic industry frequently refers to these three primary geo-racial hair types: African type hair originates primarily from south, west, or central Africa and the donors with a few exceptions tend to have heavily pigmented skin. Asian type hair originates from mid-eastern and south East Asia and the donors tend to have light to medium skin pigmentation. Caucasian hair originates from northern Europe or North Africa and the donors tend to have lightly pigmented skin, but some may have heavily pigmented skin. So, the influence of geography is recognized and persists in this important classification because the names of two of these three groups still retain their geographic origin.

These geo-racial groups will be referred to frequently in the sections involving hair fiber shape focusing on fiber diameter, ellipticity and hair fiber curvature in Chap. 9. Fiber curvature and cross-sectional shape as well as pigmentation variations of human scalp hair are largely controlled genetically. These fiber shape characteristics control much of the cosmetic and physical behavior of human hair. Therefore, geo-racial information on hair characteristics can and has been useful to the cosmetic scientist, although a century from now it will likely be less useful than the hair characteristics themselves.

Other classifications such as by curvature type will ultimately become more important to cosmetic science than the three geo-racial groups because curvature is so important to all cosmetic hair assembly properties as discussed in Chap. 10. Consider the fact that the cosmetic behavior of scalp hair of a Caucasian of Curly type IV hair by the Segmentation Tree Analysis Method (STAM) [2] (see the section entitled, *Measuring Hair Fiber Curvature* in Chap. 9) has more in common with Curl types IV of the African and Asian groups than with a curl Type I or II of their own geo-racial group. The commonality is in the way their hair behaves with regard to the more important cosmetic hair assembly properties described later in Chap. 10.

During the latter days of this century and the next, populations of Curl types III, IV and V will likely increase and Curl types I and VIII will decrease. So, in the future we must learn to type hair even better by its physical characteristics and become more quantitative with regard to its relationships to its important cosmetic hair assembly properties. Table 3.1 summarizes the general qualitative characteristics of the scalp hair of the three major geo-racial groups.

Table 3.1 Hair fiber characteristics by geo-racial group

Fiber characteristics [3, 4]				
Geo-race	Coarseness	Curvature	Cross-Sectional Shapte	Color
Caucasian	Fine	Straight to curly	Nearly round to slightly oval	Blond to dark brown
African	Coarse	Wavy to wooly	Slightly oval to elliptical	Brown-black to black
Asian	Coarse	Straight to wavy	Nearly round to slightly oval	Dark brown to brown-black

See Fig. 9.18

3.2 The Genetics of Hair Form: Hair Diameter and Curvature

3.2.1 Evolution to Hairless Bodies, Dark Skin and Highly Coiled Scalp Hair

The current ice age began about 2.6 million years ago producing a large scale climate change across the earth. Along with colder temperatures was a decline in rainfall. The densely wooded areas that our early ancestors occupied became tropical or sub-tropical grasslands with scattered trees and drought-resistant undergrowth. Consequently, the fruits, tubers and seeds and fresh water that these vegetarian hominids thrived on became scarce.

So, these vegetarians had to change their lifestyle, relocate and mutate to survive. They became hunters and fishermen traveling longer distances in search of food and water [5]. The elevated activity required for hunting and traveling for food and water increased the risk of overheating. So, this hominid adapted by losing its chimpanzee-like body fur. It developed many more sweat glands that were more efficient (for cooling) over most of its body compared with its chimpanzee-like ancestors. Montagna [6] explained that the sweat glands of fur bearing chimpanzees and gorillas do not respond to heat stimulation as in humans. Equally important, our ancestors' hairless skin became highly pigmented to protect against over-exposure from the sun in the tropics. They developed hair on the head that was highly coiled with a longer life cycle and therefore of greater length than the head fur of their predecessors.

Rogers et al. [7] concluded from studies of the human MC1R gene, involved in skin and hair pigmentation, that primitive humans lost most of their body hair by before 1.2 million years ago. Rogers et al. concluded that loss of fur had to occur before dark skin pigmentation because the specific variant of the MC1R gene that is always in dark skinned Africans originated about 1.2 million years ago.

Jablonski and Chaplin [8, 9] explained that skin color tends to correlate with latitude or the region of the earth that determines the intensity of UV radiation. These two scientists explained this effect by the fact that dark skin protects against the breakdown of folate which is essential for fertility and fetal development. Dark skin also protects against other but lesser effects with regard to reproductive success

such as protection of sweat glands, from UV damage [8], and protection against skin cancers. Jablonski and Chaplin explained further that humans in different geographical regions have evolved to be dark enough to protect folate, in the blood stream, from decomposition by UV-A radiation yet light enough to allow sufficient UV in the skin to catalyze the production of vitamin D, an essential vitamin for maternal and fetal bones. Furthermore, skin color through tanning is highly adaptive and can change at a faster rate than hair form or hair color.

3.2.2 Helpful Websites for SNP Nomenclature and Its Relationship to Hair Form and Pigments

Single nucleotide polymorphisms (SNP's) are mutations or changes that occur in a gene at a specific location. The nomenclature for SNP's in the scientific literature is variable and complex. Therefore, I recommend the following website as helpful for reading different papers dealing with SNPs because of the many different ways that gene mutations are described: www.hgvs.org/mutnomen/recs.html.

For example, sometimes a coding for the DNA sequence is used which is usually but not always described with a "c." beginning, for example (c.76 A > T) means that nucleotide 76 which was Adenine has been replaced by Thymine. Sometimes the coding is for the corresponding RNA sequence change which would be (r.76 a > u) which means that at nucleotide 76 Adenine has been replaced by Uracil. However, more frequently the coding for the protein sequence change will be designated. In that case, the coding would be (p.Lys76Asn) or p.K76N or K76N or 76N which means that at position 76 the amino acid Lysine has been replaced by Asparagine.

Another helpful website is: www.ncbi.nlm.nih.gov/sites/entrez?db=snp.

Much information can be obtained from this website including information for the DNA change, the RNA change and the protein change and much more from the rs number.

The important thing to remember in all of this discussion is that we are looking for changes in specific genes at specific locations that create changes in the proteins that are derived from these genes. Further, these proteins play a significant role in accelerating or retarding enzymatic or non-enzymatic reactions such as pH control, or the transport of key ingredients involved in the biosynthetic scheme for the formation of hair pigments, hair form or any other trait. In the case of hair pigments, oftentimes the number and size of the melanosomes will be determined and these will ultimately become hair pigment granules.

To date, more than 100 SNP's in 24 genes have been shown to be involved in hair, skin or eye color of humans and many more in mice. Now this is just hair color. Hair and skin color are closely related in a number of ways, however, there are differences too. For example, both hair and skin pigments are formed in melanocytes in structures called melanosomes. Hair and skin pigments both involve

many of the same genes. Schwan-Jonczyk [10] has shown that melanin granules in hair from people of African descent are larger than those from East Asians which are larger than those from light haired blonde or red haired Europeans. In skin, melanin is produced in melanocytes similar to those in hair. The melanocytes in African skin appear similar to those in Europeans but they are much more reactive and the melanin granules that are formed are larger and more numerous in Africans [11] analogous to those in hair.

Among the several associations between hair color and skin color are the following: Red heads are almost always fair skinned. However, the reverse is not generally true; very light hair people normally have very light skin, however the reverse is not generally true; and dark skin people normally have dark hair, however the reverse is not commonly true.

One of the most important differences between hair and skin pigmentation has been pointed out by Slominski and Tobin [12]. For example, Slominski and Tobin [12] described that melanogenesis in hair coordinates with the hair cycle and is affected strongly by age which ultimately involves the graying of hair. On the other hand, skin melanogenesis is continuous not cyclic and is not as strongly affected by age. In hair follicles, melanogenic activity is directly related to the anagen stage of the hair cycle [12]. In the telogen follicle, melanocytes are mitotically quiescent. The complex and large number of biological controls of melanogenesis are summarized in this paper by Slominski and Tobin [12]. These same scientists suggested that a small number of melanocytes in a single anagen cycle produce enough melanin pigments for a hair shaft of one or more meter or longer. Furthermore, single scalp hair follicles continue to produce hair pigments for about 7–15 cycles before the onset of graying. Graying is due to a reduction of the activity of melanocytes in the hair bulb. See this paper by Slominski and Tobin [12] for additional details on the mechanism of melanogenic activity and graying.

3.2.3 Evolution of Coiled Scalp Hair to Straighter Hair Forms

The hair of the people indigenous to Africa today is highly coiled to kinky and highly elliptical. This hair type was developed several hundred thousand years before these hominids migrated out of Africa. This highly coiled hair continued to be the dominant hair form up to the early migrations out of Africa about 50,000 years ago [13, 14]. A primary reason for highly coiled and longer hair on the scalp in hot tropical high ultraviolet (UV) Africa was to provide a protective insulating layer to the head to help prevent overheating of the brain [8]. Thermal protection of the head was important because prior to these migrations, the brain size of this hominid increased by a factor of more than two. Furthermore, the head (in addition to the shoulders) is the most directly exposed part of the body to thermal and UV radiation for a bipedal upright animal and thermal protection of the brain is much more important than for the shoulders.

Highly coiled hair was preferred over straight hair in the tropics because coiled hair allows more rapid loss of water from the scalp than straight hair. This effect is because straight hair fibers mat together with water which inhibits evaporation, and thus inhibits cooling. Highly coiled and longer hair also provides a more effective thermal insulating layer to the ever increasing brain size. This hominid continued to develop in its behavior, but changed little in skin and hair development for the next few hundred thousand years.

Straight, thicker more round hair evolved in the Far East but wavy to straight, less elliptical hair evolved in Europe (less elliptical than African hair). We will speculate on the advantages of straighter hair in cold climates as possible reasons for its evolution; however it is possible that straight hair was linked to another property like teeth or sweat glands or skin pigmentation and straighter hair just went along for the ride in a process called phenotypic hitchhiking [15].

One possible advantage of straight to wavy hair in cold climates is that straight hair grows longer in length than highly coiled African hair primarily because of the fragility of the latter type of hair. Straight hair hangs down over the neck and the sides of the head and ears to cover those body parts more effectively. Therefore, longer straight hair that grows fast provides better thermal protection to the neck and the ears than highly coiled hair. Insulation of the neck (analogous to a scarf) facilitates thermal regulation of the upper spinal cord, while the ears are one of the most vulnerable parts of the body to frostbite. Tobin and Paus [16] described the following advantage to long straight hair and attributed this rationale to Hardy. The early migrations of our species to the Far East and Europe occurred along the seacoast, more so to the Far East. Therefore, these migrants survived on a diet high in seafood which contains toxic metals which bind to melanins in hair. Therefore toxic heavy metals can be detoxified quickly by selectively binding to melanin in hair which could provide a selective advantage for longer rapidly growing, melanin rich, and straight scalp hair as in Far Easterners.

Highly coiled hair is also more effective in scattering radiation and minimizing its contact with the skin an advantage only in the tropics. Iyengar [17] proposed and showed that hair fibers to some extent can function as fiber optic strands transmitting light to the melanocytes. Furthermore, coiling in optical strands interferes with light transmission. But, whether or not straight hair fibers can function sufficiently to transmit a meaningful amount of UV to the skin to facilitate vitamin D production in clothed humans in northern latitudes remains to be seen. There is no agreement today of whether hair form has occurred by natural selection or if it is coupled to another trait controlled by selection. But, its geographic specificity does lead one to believe that natural selection was somehow involved.

3.2.4 The Genes and SNPs Involved in Hair Form

The people of Japan, China and Amerindians have been shown to have a mutation involving a simple substitution in the EDAR gene (sometimes referred to as

1540T/C or 1540C or 370A) which has been associated with hair thickness of East Asian and Amerindian populations [15, 18, 19]. In addition, Fujimoto et al. [20] determined that the FGFR2 gene is also associated with hair thickness in East Asian populations. Equally important, Mou et al. [18] demonstrated that elevation of EDAR activity via this EDAR mutation in transgenic mice decreases the number of kinks in the hair fibers as well as increasing fiber diameter. Therefore this variant gene is involved in producing straighter-more coarse hair in East Asian populations.

This EDAR gene substitution does not occur in Africans and it is at very low frequency in most of the people of Central/South Asia, Europe and the Middle East as shown by Bryk et al. [15] and Fujimoto et al. [19]. As of this writing, I have not been able to identify whether or not this substitution occurs to a significant degree in the people of India. However, I suspect it only occurs in a small percentage via the Tibetan-Burma population in the north-eastern part of India. This conclusion is based on the fact that the curvature of the main population of India tends to be more Caucasian-like than East Asian and hair diameter studies on small numbers of people from India suggests that Asiatic Indians do not have hair as coarse as East Asians.

The straight hair of Europeans and East Asians appears to have occurred independently, analogous to the independent evolution of light skin in Europeans and East Asians after these two groups of humans separated in their respective migrations. Migrations to Europe are believed to have occurred about 40,000 years ago, a few thousand years after migrations to the Far East. As indicated, the thick-straight hair of East Asians is linked to the Asian specific allele variants of the EDAR and FGFR2 genes [19, 20]. These gene variants are either not in or at very low frequencies in the hair of Europeans [15]. However, Medland et al. [21] demonstrated an association of the trichohyalin gene with straight hair in Europeans. Furthermore, these trichohyalin gene variants are highest in frequency in Northern Europeans and are specific to populations of Europe and western-central Asia. Medland et al. suggested that in this regard, these trichohyalin gene variants "parallel the distribution of the straight-hair EDAR variant in Asian populations".

The geographic specificity of the EDAR gene for hair form in combination with the trichohyalin gene variants in Europe and the Middle East support the East Asian and West Eurasian Sweeps hypothesis suggested by Coop et al. [22]. The EDAR gene is at high frequencies in Chinese, Koreans, and Japanese and Amerindian populations consistent with the geographic migrations of these populations and contributed to the hair form of the hair type we call Asian. In addition, the trichohyalin variants in Europeans and Middle Easterners are consistent with the migrations of these populations as suggested by Coop et al. and contributed to the hair form of the hair type that we call Caucasian. Also see the next section in this Chapter entitled, *Hair Pigmentation and Genetics*.

Another useful study involving hair form was conducted by Eriksson et al. [23] where 10,000 European subjects were surveyed with a questionnaire for 22

common traits including hair curl, hair color and red hair (red to not red on a scale of 4). Hair curl was evaluated with 6° of curl based on a verbal description with accompanying photographs. After the questionnaire saliva samples were taken from each subject and tested for 580,000 SNP's. These data were then tested for associations. This study revealed four genes with significant association with hair curl in Northern Europeans. Among these four genes was the rs17646946 SNP near the Trichohyalin gene (TCHH), the minor allele being associated with straighter hair and first implicated with hair curl in Europeans by Medland et al. [21]. The rs7349332 SNP near WNT10A, the minor allele (T) was associated with slightly curlier hair and rs1556547 near OFCC1 was also associated with straight hair.

Shimomura et al. [24] also suggested with some evidence that the IRS specific epithial keratin genes KRT71-74 may be involved in the determination of hair texture, particularly with regard to coiled hair of different mammalian populations.

3.3 Hair Pigmentation and Genetics

We know that highly pigmented hair is both geographically/racially related (geo-racially) suggesting genetic involvement. For example those of African and Asian origin tend to have larger amounts of eumelanin in their hair while those of Caucasian extraction especially originating from Northern Europe tend to have less pigment such as eumelanin and more pheomelanin. Schwan-Jonczyk [10] suggested that melanin granules are ovoid or spherical and that the size and density of the granules are smaller and lower in Caucasians; that is the total melanin content and type of melanin [eumelanin (brown-black) versus pheomelanin (yellow-red)]. She concluded that Black African hair contains large agglomerated eumelanin granules about 0.8 μm along their major axis, while Japanese hair has smaller melanin granules about 0.5 μm and blonde European hair contains even smaller primarily pheomelanin granules about 0.3 μm. These observations on melanin size and race are consistent with those by Swift [25] for African versus Caucasian hair. Thus, the intensity or depth of color is related to both the size of the melanin granules and the total melanin content (the melanin granule density) while the proportion of eumelanin to pheomelanin is believed to be involved in determining the shade of hair color.

Melanins are synthesized in melanocytes (melanin producing cells) from the amino acid tyrosine and pheomelanin from tyrosine and cysteine and packaged into melanosomes in the melanocytes. The melanin containing melanosomes ultimately become melanin granules after being transferred into keratinocytes, cells that form the shaft of hair fibers. A more complete discussion of the biosynthesis and proposed structures for hair melanins is covered in Chap. 5.

3.3.1 Melanin Granules of Different Hair Types

From cross-sections of African hair versus dark-brown Caucasian hair the melanin granule density clearly appears higher in African hair. Two papers on melanin granule size and density in human hair, both Japanese papers by Kita et al. [26, 27], indicated a higher melanin density in the outer cortex versus the inner cortex. This melanin distribution effect is also typical of Caucasian and African hair. These scientists found no difference in melanin granule size and density in infant hair versus 20–30 year olds, but significant differences at age 60–70 wherein the minor axis of the melanin granules was smaller than for the other age groups. The density (number per square cm) of the melanin granules was lower at the advanced age [26, 27].

There is a wider range of natural pigment shades for Caucasian hair than for any other geo-racial group. We know that several genes are involved in the production of hair pigments. Furthermore, many of these genes function differently in different populations. But, the primary mechanisms of these genes are to control the size, aggregation state and the ratio of eumelanin to pheomelanin in the melanosomes which ultimately become the pigment granules of hair fibers.

3.3.2 The More Important SNPs and Genes for Hair Pigments

In 2010 Valenzuela and Brilliant [28] described 75 SNP's in 24 genes that have been associated with human or animal pigmentation for hair, skin and or eye color. These scientists analyzed these 75 SNP's by ANOVA and concluded that 31 were from 13 genes associated with either total melanin content or the ratio of eumelanin to pheomelanin in human hair fibers [28]. Multiple regression modeling by Valenzuela and Brilliant considering SLC24A5, SLC45A2 and HERC2 for total scalp hair melanin accounted for 76.3% of the variance. Modeling for the ratio of eumelanin to pheomelanin considering SLC24A5, SLC45A2 and MC1R accounted for 43.2% of the variance. So, these four genes (SLC24A5, SLC45A2, HERC2 and MC1R) are clearly among the more important genes to hair coloring, see Tables 3.2 and 3.3. However, since three of these genes, SLC24A5, SLC45A2 and MC1R explain less than half of the variance for the ratio of eumelanin to pheomelanin (the shade or color factor) and the fact that other genes are likely linked to the action of these genes highlights the fact that genes, in addition to these four, are obviously important to hair color.

Table 3.2 summarizes data from a few of the more important genes that have been implicated in pigmentation of human hair. At least three of these genes are believed to be involved in membrane transport. SLC45A2 produces the membrane-associated transporter protein (MATP) which has been suggested by Yuasa et al. [38] to be involved in the transport of melanosomal proteins to the melanosomes. The SLC24A5 gene (NCKX5) which stands for $Na^+/Ca^{++}/K^+$ exchanger 5 has been

Table 3.2 Some important genes/SNP's involved in hair color for major geo-ethnic groups

		Frequencies for populations of these groups (%)		
Gene	SNP/allele variant	East Asians	Africans	Caucasians
SLC45A2	rs16891982 (374L)	98.9 [29, 30]	98.9 [29]	1.7 [29]
	rs16891982 (374F)	1.1 [29, 30]	1.1 [29]	98.3 [29]
SLC24A5	rs1426654A = Thr^{111}	1.9 [29]; 36₮ [31]	4 [31]	97.8 [30]; 100₮ [31]
	rs1426654G = Ala^{111}	93–100 [32]	93–100 [32]	0₮ [31]
OCA2/HERC2	rs12913832C = i86			74 [33]
	rs12913832T			26€ [33]
P gene	rs1800414 (H615R)	44 J [34]; 54 J [35]	100 [34]	100 [34]
		54 C [35]		
ASIP	rs6058017G (g.8818G)	28 [36]	80 [36]; 60 [29]	12 [36]; 24 [29]
	rs6058017A		39.6 [29]	75.8 [29]
MC1R	rs885479 (R163Q)	75.5 [37]	0 [37]	4.6ʃ 1.6%€ [37]
	rs1805007 (R151C)		0 [37]	5.8 [37]

ʃ Northern Europeans, € Southern Europeans, ₮ Italians, *J* Japanese, *C* Chinese

suggested by Lamason et al. [32] to regulate the Ca^{++} concentration in the melanosomes. In addition, the P protein which is encoded by the OCA2 locus is another multi-transmembrane protein involved in the formation of melanin. Its function is unknown at this time, however, it has been suggested by Chen et al. [39] to involve the transport of tyrosinase (the enzyme involved in the formation of melanin pigments from tyrosine). Variants of the MC1R and to some extent the ASIP genes have been shown to be involved in determining the ratio of eumelanin to pheomelanin in the melanosomes.

Earlier in this chapter in the section on hair form entitled, *Evolution of Scalp Hair to Coiled and Straight Hair Forms*, the concept by Coop et al. [22] of East Asian and West Eurasian Sweeps was presented. This concept links genetics to geographic migrations out of Africa. The first migration was to the Far East (China, Korea, Japan and Mongolia) then to the Americas (Amerindians). The second migration was through the Middle East and then westward to Europe forming the Caucasian group. The p.A111T (THR^{111}) variant of the SLC24A5 gene for light skin and hair is at a high frequency in Europeans (Caucasians) and at low frequencies in East Asians and Africans [22, 31] supporting the East Asian Sweep, see Table 3.2. While the R163Q variant of the MC1R gene for dark hair is at a high frequency in East Asians and Amerindians and at low frequencies in Europeans and Africans supporting the West Eurasian Sweep [22, 37], see Table 3.2.

Han et al. [40], in 2008, conducted a genome-wide study among more than 10,000 European males and females. This study revealed 38 SNPs associated with hair color. The involved gene variants were located on six different chromosomes and involved eight different genes. Therefore, as Sturm [29] suggested, earlier anticipation that human pigmentation is dominated by a few TYR gene mutations that could control the formation of melanins has been shown to be a gross

Table 3.3 Genotype and hair color associations for variants in Southern Europeans [33]

Hair color by the percentage of the subjects of that color								
Gene/SNP	AA change	Genotype	N (%)	Red	Lt blonde	Lt brown	Dk brown	Black
SLC45A2/								
rs16891982	F374F	F/F	184 (81.4)	12	14.2	14.8	48.6	10.4
	F373F/F374L	F/L	40 (17.7)	5.1	7.7	7.7	56.4	23.1
	F374L	L/L	2 (0.9)	50	0	0	50	0
rs26722	E272E	E/E	211 (93.3)	10.5	12.9	14.3	51.4	10.9
	E272E/E272K	E/K	14 (6.2)	15.4	15.4	0	30.7	38.5
	E272K	E/K	1 (0.4)	100	0	0	0	0
SLC24A5/								
rs1426654	T111T	T/T	244 (99.1)	11.3	13.1	13.5	49.6	12.6
	T111T/T111A	T/A	2 (0.9)	0	0	0	100	0
	T111A	T/T	0 (0)	–	–	–	–	–
OCA2-HERC2/								
rs12913832		[a]C/C	57 (25.3)	8.8	28.1	17.5	40.4	5.3
		[a]C/T	108 (48)	11.2	11.2	15.9	51.4	10.3
		[a]T/T	60 (26.7)	13.6	1.7	5.1	55.9	23.7
MC1R/								
Homozygous wild type₸		+/+₸	86 (38.1)	0	10.5	20.9	47.7	20.9
Heterozygous wild type		€r/+	69 (30.5)	0	14.5	10.1	63.8	11.6
		€r/r	12 (5.3)	0	0	8.3	83.3	8.3
		¥R/+	26 (11.5)	20.8	16.7	16.7	41.7	4.2
		¥R/r	13 (5.8)	38.5	38.5	0	23.1	0
		¥R/R	20 (8.8)	75	5	0	20	0

[a]Nucleotide changes not amino acid changes

₸Wild type is + and is also referred to as consensus or the most common genotype; €r is V60L, V92M and R163Q; ¥R is R142H, R151C, I155T, R160W and D294H

oversimplification. Table 3.3 has been modified from a similar but larger table tabulating effects on skin and eye pigmentation as well as hair pigmentation by Cook et al. [33].

Another interesting study was conducted by Eriksson et al. [23] where 10,000 Northern European subjects were surveyed with a questionnaire for 22 common traits including hair color (blonde to black on a 7 point scale) and red hair (red to not red on a scale of 4 choices ("before I went gray, if I am gray now")). The hair color results revealed that rs12913832 of the OCA2/HERC2 region explains 12.2% of the variance for hair color in Northern Europeans, rs16891982 of SLC45A2 explains 2.7% of the variance and several SPN's of MC1R and two of ASIP are involved in red versus non-red hair color, results consistent with other studies.

Masui et al. [34] concluded that the MC1R gene and the P gene can serve as indicators of the origin of individuals in some populations. These scientists started with 18 SNP's, 11 from the MC1R gene and 7 from the P gene and narrowed down to 4 SNP's, the R163Q SNP from MC1R (rs885479) the IVS5+1001, IVS13+113 and H615R (rs1800414) from the P gene. Masui et al. combined the P gene SNP's versus the R163Q (rs885479) into a factor called CG which showed clear distinction between Asian populations (Japan, China, Korea and Mongolia combined) versus European or African populations. Interestingly, there appears to be a small distinction between Japanese versus the Chinese, Korean and Mongolian populations combined also.

Of the several genes involved in human hair, skin and eye color, the MC1R gene has shown the largest number of mutations and has been studied most thoroughly. In 2008, Savage et al. [37] published a paper describing allele frequency data on 55 SNP's of the MC1R gene from seven geographic populations of 2,306 persons. Savage et al. found a frequency of 75.5% for the R163Q protein (c.488 G > A allele variant; rs57758262) among 343 Asians including 282 Japanese and 50 Chinese with frequencies less than 5% for any other group for this same protein-allele. The next MC1R allele with a high frequency was for the T314T protein produced by the c.942 A > G allele; a dark hair allele with a frequency of 44.4% for the African population of 117 subjects 13.3% for the Asian group, 13.2% for the Asiatic Indians and 18.75% for the Papua New Guinea population [37].

A variety of different hair colors can be produced by different genotypes of the MC1R alleles. Among the MC1R alleles of Table 3.3, the homogeneous wild type (the consensus or most common) produces the highest percentage of black hair. Of the MC1R variants, the r variants do not produce red hair, but only dark brown to blonde hair. The heterozygous wild type with r and the homogeneous r/r genotypes produce from 75% to 92% dark brown to black hair. On the other hand, the R variants produce increasing percentages of red hair from 21% to 75% of the subjects with the highest percentage for the R/R homozygous subjects.

Lu et al. [41] showed that the MC1R gene can function to produce lighter shades of pigment via agouti-signaling involving another gene variant that produces a protein that antagonizes or inhibits the α-melanocyte stimulating hormone (α-MSH). Valverde et al. [42] in 1995 concluded that mutations of the MC1R gene are involved in red hair formation in humans and the mechanism involves increasing the ratio of pheomelanin to eumelanin in the melanosomes. This type of genetic variation is highest among Europeans with red hair and fair skin [43]. Branicki et al. [43] determined that at least 5 MC1R variants are involved in red hair production: C451T (rs1805007) providing an amino acid change of p.R151C, C478T (rs1805008) providing an amino acid change of R160W, C252A, (rs1805006) providing an amino acid change of D84E, G425A providing an amino acid change of R142H and G880C providing an amino acid change of D294H (rs1805009).

The major role was played by the first two of these gene variants for people of Polish descent and has been show by Savage et al. [37] to be at higher frequencies among European and US populations. The C451T variant has been shown by Savage et al. to occur at 5.6% in Northern Europeans, at 3.16% in Southern

Europeans and at 6.42% in the United States while the C478T variant at 8.3% in Northern Europe, at 1.9% in Southern Europe and at 7.2% in the United States. Box et al. [44] showed that the G178T variant (rs1805005) that provides an amino acid change of p.V60L is associated with fair or blond and light brown hair. This variant has been shown by Savage et al. [37] to occur at a frequency of 10.7% in Northern Europeans, at 15.75% in Southern Europeans and at 13.21% in the United States.

Savage et al. [37] and others described that in most regions of the genome there is greater genetic variation in African populations than most other populations. But the MC1R gene is an exception to this rule of thumb. This exception occurs because of the greater variation in hair pigments and skin pigments of people of European descent versus those of African descent.

Kanetsky et al. [45] provided evidence that the ASIP gene is also involved in the production of dark hair and brown eyes in European Americans. Bonilla et al. [46] suggested that the specific SNP of the ASIP gene described as g.8818A>G (SNP# rs6058017) is believed to function by producing a protein that binds to MC1R and promotes formation of eumelanin and darker skin color in African Americans. Zeigler-Johnson et al. [36] demonstrated that the allele of ASIP g.8818 G is involved in this type of agouti-signaling to promote eumelanin production and occurs at a high frequency (0.80) in West Africans, at 0.62 in African Americans, 0.28 in East Asians and at a frequency of 0.12 in European Americans. Harding et al. [47] concluded that the MC1R gene is "under strong functional constraint in Africa" and any change would be harmful from an evolutionary perspective.

Branicki et al. [48] demonstrated that the SLC45A2 gene also called MATP for membrane associated transporter protein is involved in hair color and in particular the L374 allele significantly increases the likelihood of black hair color in Europeans. The L374F (rs16891982, c.1122C > G) polymorphism of SLC45A2 has been suggested by Yuasa et al. [38] as a possible important factor in hypo-pigmentation in Caucasian populations. This SNP occurs at a high frequency in German, French and Italian populations and is virtually absent in African and East Asian populations [38]. It also occurs at low frequencies in Indians from New Delhi (14.7%) and Bangladeshi (5.9%) important populations of India.

The SLC24A5 gene has been found to affect pigmentation in zebrafish and humans and has been implicated in hair color by Lamason et al. [32] and confirmed by Valenzuela and Brilliant et al. [28]. The frequency for the p.A111T (rs63750629, c.331G > A) has been shown to be high in European populations (0.975) and low in Chinese (0.019) by Soejima and Koda [30].

The HERC2 gene sometimes called OCA2/HERC2 (Table 3.2) has been suggested by Sulem et al. [49] to be involved in expression of the OCA2 gene that reduces pigmentation in the hair of Europeans. The rs12913832 allele of the HERC2 gene has been shown by Valenzuela and Brilliant [28] to be involved in hair pigmentation and by Eiberg et al. [50] to be involved in brown eye color by inhibiting OCA2 expression. The OCA2 gene is involved in the most common form of albinism. Rebbeck et al. [51] determined that mutations of the P gene are also involved in eye color by association of these mutations with the OCA2 gene.

3.4 Some Other Hair Traits Related to Genetics

Shimomura and Christiano [52] reviewed genetically involved hair diseases in a comprehensive review entitled, *Biology and Genetics of Hair*. I refer the interested reader to this review for a description of several more hair diseases with genetic involvement than are described in this chapter. The most interesting to this author are the possible connections to the development of "normal" non-diseased hair such as those involved in pigmentation (in the previous section) and hair form. One example is the paper by Shimomura et al. [24] suggesting the possible involvement of IRS specific epithial keratin genes KRT71-74 in the determination of hair texture, particularly with regard to coiled hair of different mammalian populations.

With respect to androgenetic alopecia, the most common form of hair loss, several genes have been implicated. Hillmer et al. [53] demonstrated that the androgen receptor gene (AR) on the X chromosome is the primary requirement for early-onset androgenetic alopecia. The fact that location of this important gene is on the X-chromosome signifies the significance of the maternal line to androgenetic alopecia. A genome wide linkage study by Hillmer et al. [54] of 95 families of German descent provided evidence for linkage to chromosome 3q26. The susceptibility to male pattern baldness has also been shown to relate to five SNPs on chromosome 20pll by Brent Richards et al. [55] and Hillmer et al. [56]. This study by Hillmer et al. [56] suggested no interaction with the androgen receptor on the X-chromosome suggesting an androgen independent role from the product of these genes. Chromosomes 5 and 2 which harbor genes encoding the two 5α-reduction isoenzymes were found by Ellis et al. [57] to not be associated with male pattern baldness, therefore, the authors suggested that a "polygenic etiology should be considered" for the role of 5α-reductase in male pattern baldness.

Ahmed and Christiano et al. [58] identified a hairless gene (hr) on chromosome 8p12 that is associated with alopecia universalis in humans and Nothen et al. [59] have mapped the locus on chromosome 8p21-22. Martinez-Mir and Christiano et al. [60] have conducted a genome wide scan for linkage to alopecia areata implicating at least four susceptible loci on chromosomes 6, 10, 16 and 18 using more than one statistical approach.

Heywood et al. [1] working with hair from 292 female Caucasians characterized the hair of these subjects by amino acid analysis, dry tensile elastic modulus, two-dimensional electrophoresis of hair protein extracts and the perception of hair quality by the panelists themselves. The results from protein analysis provided a string of 66 kDa proteins that correlated with higher perceived hair quality. These scientists also noted a decrease in the low molecular weight (14–29 kDa) proteins with the use of hair coloring products.

Amino acid analysis revealed that the perception of hair quality was associated with higher levels of the amino acids serine and threonine. Higher elastic modulus was significantly higher in hair of higher perceived quality. Serine is an amino acid that occurs at very high levels in the ultra high sulfur proteins of hair. There are also threonine rich keratin associated proteins [61]. Therefore, higher concentrations of

these amino acids may suggest higher concentrations of the ultra high sulfur proteins or related keratin associated proteins which are likely under genetic control. From these results, these scientists hypothesized that hair quality is likely to be genetically determined.

3.5 Hair Abnormalities

Abnormalities in this section are classified as diseases involving growths on the hair and diseases of genetic origin that affect the structure of the hair fiber. Lice and Piedra are discussed in the last part of this section because they produce nodules on the hair shaft as well as affect the scalp in contrast to dandruff, a disease primarily of the scalp discussed in Chap. 6.

The sections in Chap. 1 entitled *Intermediate Filaments* and in Chap. 2 entitled *Type I and Type II Keratin Proteins (IF Proteins) of Human Hair* discusses only the Type I acidic keratins and the Type II neutral-basic keratins that are essential structures of the human hair fiber. Langbein and Schweitzer [62] described that IF proteins of human hair are involved in a few diseases such as monilethrix and certain hair follicle derived tumors. Six different types of IF proteins are described in the review paper on intermediate filaments and disease authored by Eriksson et al. [63]. Type III IF proteins include vimentin and desmin, Type IV IF proteins include nestin, synemin and the neurofilament triplet proteins, Type V IF proteins are the nuclear lamins and Type VI IF proteins of the eye lens cell are not considered in the discussion in this current Chapter. Nevertheless IF family members all share a central helical coiled-coil rod with variable Nitrogen and Carbon terminal groups that provides huge structural diversity. The IFs of human hair fiber are structural proteins while the other IF types are located in epithelia, muscle, neuron and eye lens cells. To date, the IF proteins of human hair fiber involve a few defective keratins in hair fibers and a few hair follicle derived tumors [63]. Numerous diseases of other tissues involve these other Types of IF proteins and include neurodegenerative diseases such as Lou Gehrig's disease, and Parkinson's disease, muscular dystrophy, liver disease and cataracts [63] all connected in some way to Intermediate Filaments.

Monilethrix, pili torti, pili annulati, trichorrhexis nodosa, Menke's disease and trichothiodystrophy are somewhat rare structural anomalies in human hair under genetic influence. The structural changes occurring in these anomalies are so large that they may be observed microscopically.

Monilethrix is a congenital, hereditary disease resulting in abnormal human scalp hair. Monilethrix is also called moniliform hair or beaded hair, and it produces hair fibers with the appearance of a twisted ribbon, as illustrated by the light micrograph of Fig. 3.1. However, in spite of its casual appearance detailed examination shows that monilethrix does not exhibit severe twists and it is thus distinguishable from pili torti. This disease is also characterized by dry, fragile hair fibers. Therefore, in monilethrix, hair length generally does not exceed a few centimeters,

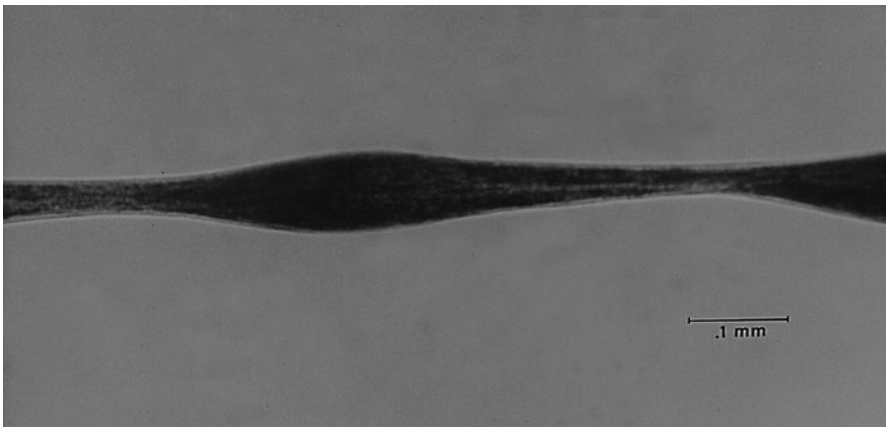

Fig. 3.1 Monilethrix, a congenital and hereditary structural anomaly of human scalp hair (Kindly provided by John T. Wilson)

particularly hair with narrow internodes. Healy et al. [64] studied two families with autosomal dominant monilethrix and excluded linkage to the type I keratin gene cluster on 17q, but provided evidence that this disorder is linked to the type II keratin cluster on 12q. Genes for basic trichocyte keratins are found on this latter gene. Congenital monilethrix produces defects in keratin intermediate filaments (hHb6 and hHb1) [62], the filamentous proteins in the cortex, see this paper by Langbein and Schweitzer [62] and the references therein. The most frequent mutations for monilethrix are E413K, E402K and E413D for hHb6 and E402K for hHb1 although other less frequent mutations have been described [62]. These mutations interfere with assembly or adhesion of the coiled coil dimers in the intermediate filaments resulting in very brittle, dry hair. Langbein and Schweitzer [62] concluded further that in addition to monilethrix those potential hair disorder candidates for the inability of mutated keratin proteins to form stable IF structures include pili annulati, wooly hair, numerous hypotrichoses and nail diseases.

Pili torti is a rare congenital deformity of the hair characterized by flattened fibers with multiple extensive twists. In some cases, the hair grows to a normal length, although frequently this deformity produces short, twisted, broken hairs presenting the appearance of stubble. Pili torti provides a high frequency of rotation (usually about 180°) and can resemble mildly affected monilethrix hair shafts (see Fig. 3.2) but its distinguishable by the severe twists of pili torti which show up better in SEM than in light microscopy see Fig. 3.3. Figure 3.3 shows three different pili torti hairs compared with one monilethrix hair. The extremely twisted hair on the left has been called corkscrew hair by Whiting et al. [65]. Price [66] identified two human DXL genes in the TDO locus (DLX3 and DLX7) and identified mutations in DLX3 in tricho-dento-osseous (TDO) syndrome patients. These genes are located on chromosome 17q21. TDO syndrome exhibits kinky curly hair, thin-pitted enamel, taurodontism and thickening of cortical bone.

Figure 3.4 illustrates Pili annulati, sometimes called ringed hair. Ringed hair is a rare hereditary condition characterized by alternating light and dark bands along the hair fiber axis described in the previous section entitled, *Medull*a. Giehl et al. [67] studied three families with 40 subjects affected by pili annulati to narrow the locus which was mapped to chromosome 12q24.34-24.33. These scientists "reduced the critical interval of pili annulati to 2.9 Mb". They also used sequence analysis to exclude mutations in the coding region of 36 potential candidate genes.

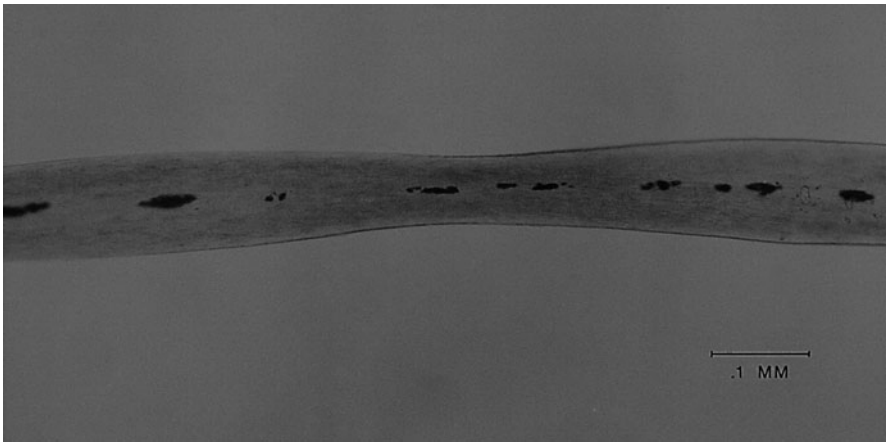

Fig. 3.2 Pili torti, an uncommon hair shaft anomaly, see also Fig. 9.12 (Kindly provided by John T. Wilson)

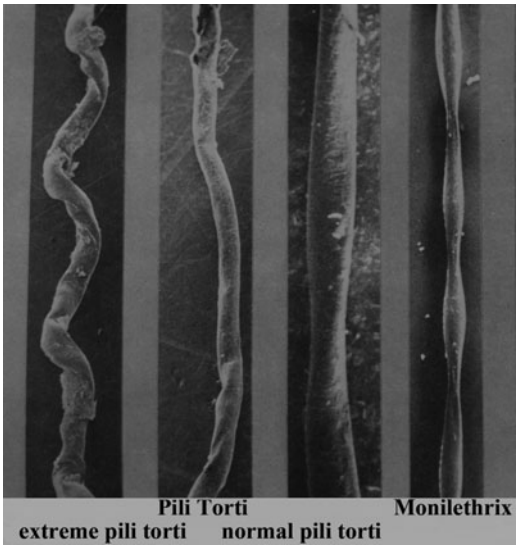

Fig. 3.3 Three different pili torti hairs and one monilethrix hair [58] (Reprinted with permission of Praeger Publishers, New York, NY)

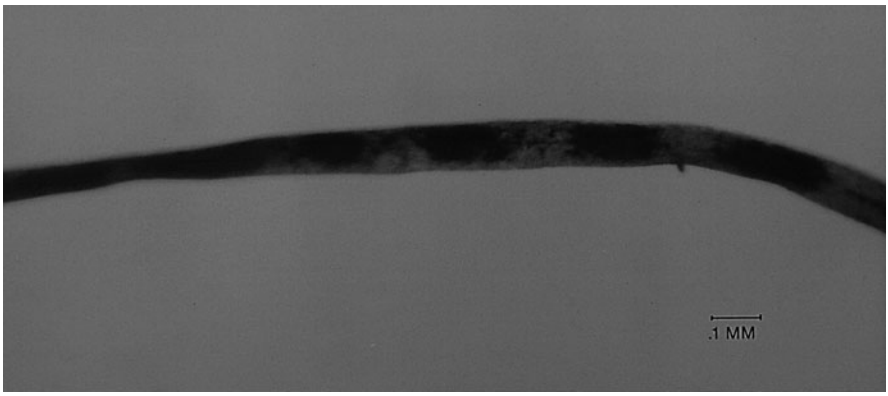

Fig. 3.4 Pili annulati (ringed hair). An uncommon inherited hair shaft anomaly (Kindly provided by John T. Wilson)

Netherton's syndrome is a skin disorder characterized by several hair shaft abnormalities two of which provide the appearance of nodes on the hair. Trichorrhexis invaginata involves the invagination of a short portion of the root of the hair into a short part of the tip of the hair providing the appearance of a node. Trichorrhexis nodosa forms the appearance of nodes on the hair provided by expansion of the cortical cell/cell membrane complex regions. These nodes are usually, but not always, fragile regions along the hair shaft. Dermatologists often refer to fragile hair as "Acquired trichorrhexis nodosa" and separate it into two disorders. Hairs with Proximal trichorrhexis nodosa break near the scalp. This condition is more common in African hair. Proximal trichorrhexis nodosa is exacerbated by hair straightening and braiding.

Distal trichorrhexis nodosa is more common in European or Asian hair with breaks occurring closer to the tips. This disease is exacerbated by chemical treatments, prolonged sun exposure and mechanical stress. It is often corrected over time and can be helped by the use of conditioners and care. Congenital trichorrhexis nodosa is a genetic disease involving a disorder of the urea cycle producing multiple nodes along the hair shaft, see Fig. 3.5. This genetic disorder occurs more often in facial hair than scalp hair, and produces bulbous type nodes appearing as irregular thickenings along the hair shaft. These nodes are actually partial fractures, which under stress crack more completely forming broom-like breaks illustrated by Fig. 3.6. Netherton's disease or syndrome has been shown by Bitoun et al. [68] to involve mutations of SPINK5 as the defective gene on chromosome 5q32 encoding the serine protease inhibitor Kazal-type 5 protein (LEKTI).

Menke's syndrome is a genetic disorder producing very kinky human hair in which the sulphydryl groups are only partly converted to disulfide bonds (about 50% oxidized) and is linked to a copper deficiency caused by a mutation in a protein involved in copper transport. Another symptom of Menke's syndrome is deterioration of the nervous system. Menke's syndrome is an X-linked recessive disorder involving a gene that encodes a copper-transporting ATPase located at Xq13 as

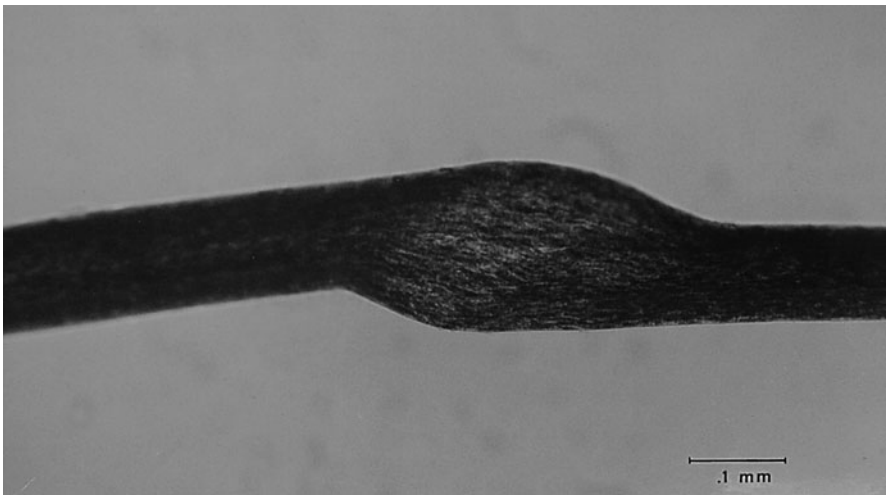

Fig. 3.5 An intact hair fiber illustrating the condition of trichorrhexis nodosa (Kindly provided by John T. Wilson)

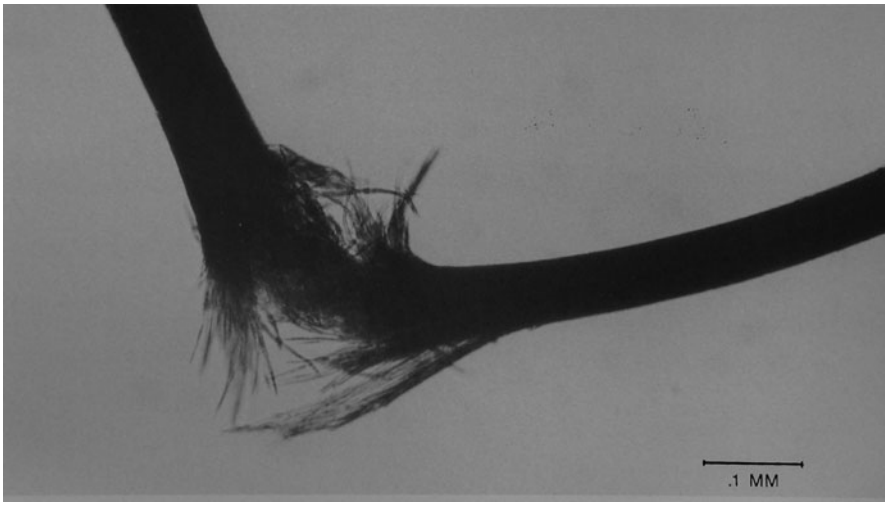

Fig. 3.6 Trichorrhexis nodosa. "Broomlike" fractures at the "nodes" are symptoms of this hair shaft anomaly (Kindly provided by John T. Wilson)

shown by Vulpe et al. [69]. Menke's kinky hair disorder occurs primarily on males because males have only one X chromosome and the probability for both X chromosomes of a female being affected is very low. Subcutaneous injections of copper if done early are sometimes helpful.

Trichothiodystrophy (TTD) is a number of syndromes affecting both the hair and the nails and other organs resulting from mutations producing sparse and brittle hair, nail dystrophy, mental and growth retardation, ichthyosis, decreased fertility and cutaneous photosensitivity. There are several forms of nonphotosensitive TTD and photosensitive TTD. Amish brittle-hair syndrome is characterized by short stature, mental retardation, hair with very low sulfur content and decreased male fertility. Other forms of nonphotosensitive TTD include Pollitt syndrome and Sabinas brittle-hair syndrome with similar clinical conditions. Nakabayashi et al. [70] determined one gene involved in nonphotosensitive TTD as C7orf11 which maps to chromosome 7p14 and is expressed in hair follicles. In TTD the hair contains only about one half the cystine content of normal hair. Such low cystine cross-link levels account for the brittleness of the hair in this disorder.

Jones and Rivett [71] described maple syrup urine disease or branched chain keto-aciduria (MSUD) as a rare genetic defect involving a lack of the enzyme that synthesizes 18-methyl eicosanoic acid from isoleucine. This enzyme is involved in a necessary biological process for eliminating excessive branched chain amino acids from the body. In MSUD, branched chain amino acids can build up to toxic levels. Some of the symptoms of MSUD are maple syrup odor in cerumen at 12–24 h after birth, elevated levels of branched chain amino acids by 12–24 h, ketonuria, irritability and poor feeding by 2–3 days and in some cases coma and respiratory failure by 7–10 days [72]. Strauss et al. [72] in their thorough review of MSUD describe three types of MSUD, the disease characteristics, diagnosis and testing and treatment as well as its genetic basis. MSUD Type I involves the chromosomal locus 19q13.1-q13.2 and the gene symbol BCKDHA and is found in certain Mennonite populations. MSUD Type II involves the chromosomal locus 6q14 and the gene symbol BCKDHB and has been found in the Ashkenazi Jewish population. MSUD Type III involves the chromosomal locus 1p31 and the gene symbol DBT.

MSUD patients lack 18-methyl eicosanoic acid in hair. In MSUD, this unique branched chain fatty acid is substituted by linear saturated fatty acids, mainly C16, C18 and C20. Smith and Swift [73] found that hair from persons with MSUD does not cleave cleanly at the Beta-Delta layers as with normal hair and therefore it provides more endocuticular failure. MSUD is described in more detail in Chapter 1 in the section entitled “The cuticle-cuticle CMC”.

Lice and Piedra are two diseases that occur primarily, but not exclusively among pre-pubertal children. Both of these diseases produce nodules on hair shafts that contain eggs for the former and spores for the latter.

Lice nodules may appear on hair on most areas of the body, such as the scalp, the eyebrows or even the pubic region (crabs). The human head louse, *Pediculus capitis*, is a very small wingless parasitic insect that survives on the blood of humans. The louse has a flattened body, about 3 mm long, with a claw on the end of each leg which it uses to cling to the hair of its host. Female lice lay whitish eggs called nits. The nits are bound to the hair of the host with an adhesive material. In most cases it is easier to find nits than adult lice because of the immobility of the former and the high mobility of the latter. Nits are generally laid close to the scalp. Since nits are “permanently” attached to the hair shaft, they can be found near the

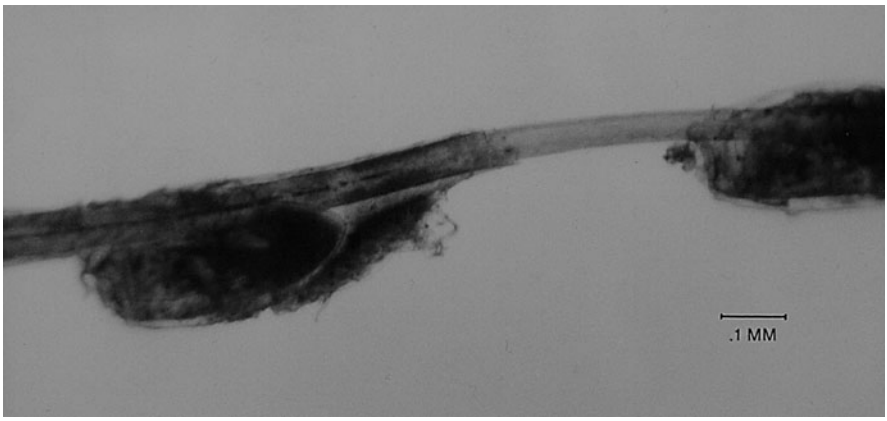

Fig. 3.7 Light micrograph illustrating empty nits of the head louse *Pediculus capitis* on a human scalp hair (Kindly provided by John T. Wilson)

tip ends of long hair from growth, after long attachment times. The eggs hatch in about a week after attachment. Three molts in only 2–3 weeks' produces a mature adult louse. Figure 3.7 is a light micrograph illustrating the empty nit sacs of the human head louse.

When the insect bites the host a small amount of a mild toxin is released. The bite usually leaves a tiny red spot that with scratching can cause larger sores. Louse infection occurs frequently and should be considered as a possible causative agent in cases of prolonged scalp itching. The resultant pruritus can lead to excoriation and secondary infection. After several bites the victims may become sensitized to the toxin. Lice are also capable of transmitting several diseases including typhus and relapsing fever.

Lice infection is usually treated by shampooing and combing frequently with a fine tooth comb to remove the nit sacs. Re-treatment in 7–10 days is essential to remove or kill the lice that hatch from the nits. Rubbing a product containing an insecticide into the hair and the scalp is even more effective. It is usually recommended to apply the treatment at night and to shampoo in the morning and then to repeat treatment in 7–10 days. Products are shampoos, crème rinses and hair/scalp creams. Leave in products are more effective than shampoos. Crème rinses are claimed to help remove nit sacs because they facilitate the comb out.

Insecticides such as permethrin, benzyl benzoate, lindane and pyrethrin have been used to treat lice. Pyrethrins are insecticides initially derived from certain species of chrysanthemum flowers. Synthetic pyrethroid insecticide is more stable with a similar activity and low mammalian toxicity and is called permethrin. Lindane (1,2,3,4,5,6 hexachlorocyclohexane) and benzyl benzoate have also been used as Pediculocides. Lice infection is spread by direct contact or by wearing the clothing of an infected person. The control of secondary bacterial infection may require an antibiotic.

Black Piedra "black stone" is caused by *Piedraia hortai*, a fungus that can affect scalp hair, and sometimes beard mustache or even body hair. This fungus penetrates

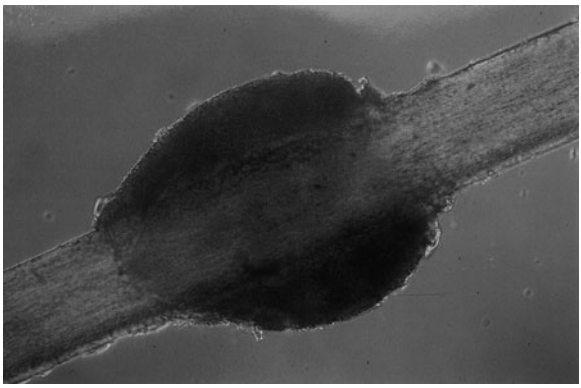

Fig. 3.8 Light micrograph of the spore sacs of the Black Piedra fungus on a human hair fiber

the cuticle resulting in adherent rough or granular black to brown nodules (see Fig. 3.8) that can be observed microscopically or even with the naked eye. These penetrating nodules can weaken the hair shaft and even lead to hair shaft fractures.

White Piedra is caused by *Trichosporin beigelii*, another fungus, and is found more often in pubic hair than in scalp hair. White Piedra can also weaken hair fibers and produce fractures. The whitish nodules from this fungus are easy to remove from the hair fiber, but are usually full of fungal spores. Black or white Piedra can be identified or diagnosed by microscopic examination or by cultures from infected hairs. Piedra usually occurs in tropical or humid climates such as tropical South America; however, white Piedra has also been identified in certain parts of Europe. Antidandruff products containing strong fungicides should be effective against Piedra. See the antidandruff section in Chap. 6 for a description of the most effective fungicides in hair products.

For additional details relevant to these hair shaft anomalies, see the review paper by Shimomura and Christiano [52] and the book edited by Brown and Crounse [74].

3.6 Hair Analysis for Drugs and Forensic Studies

Hair analysis for drugs of abuse has been described to detect cocaine [75–77], marijuana [75], nicotine [78], opiates [79] and amphetamines [78–81]. Originally drugs were extracted from the hair followed by gas chromatographic/mass spectrophotometric (GC/MS) analysis for the drug. More recently, the hair is dissolved and antibodies used in radioimmunoassay (RIA) act as specific agents for extraction/analysis [77, 82, 83]. The analysis is generally by GC/MS. Some distinct advantages exist in hair analysis over urinalysis, such as the detection of long term drug usage is more readily identified. However, drug usage over the most recent few days is not detectable by hair analysis. All analytical methods have limits. Although, hair analysis does appear to offer potential, however, the limits for hair analysis are still in the process of being defined [82].

A review of hair analysis for drugs of abuse is provided in the paper by Baumgartner [83] addressing some of these limits. Hair analysis for drugs of abuse such as ethyl alcohol, amphetamines, barbiturates, cocaine, ecstasy opiates, etc. can be determined [84]. If scalp hair is not available, hair from other areas of the body such as armpit, eyebrow, pubic or facial hair can be used; although differences in growth rates must be taken into consideration. Kelly et al. [85] examined hair analysis for three drugs, amphetamines, cocaine and cannabinoids and determined there is no bias introduced by hair color or racial effects for hair analysis of those drugs. One concern expressed in the literature for hair analysis deals with the potential for false positives created by contamination by passive environmental exposure, e.g. smoking of PCP or marijuana, etc. The review by Baumgartner speaks to this concern by pre-washing the hair to remove the passive contaminants and not the material deposited in the cortex through the bloodstream. For example, environmental contamination via passive smoke exposure should provide for only superficial sorption near the surface rather than deeply penetrated drugs taken internally.

3.6.1 Forensic Studies and DNA Analysis

Hair fibers are frequently found at crime scenes, and they are usually evaluated first for a large number of macroscopic and microscopic comparisons for identification as described by Gaudette [86, 87]. Characteristics such as color, pigment size, pigment distribution, pigment density, whether the fiber has been dyed, type of medulla, maximum and minimum diameter, type of cut at tip, length, scale count, and various cross-sectional characteristics are used in this evaluation. Such comparisons have been invaluable for either excluding or incriminating suspects in crimes. However, more recently, several newer techniques have been developed including blood group analysis [77], DNA analysis [88–95], and drug analysis (see the previous section), that together provide for even more conclusive evidence for either excluding or targeting a suspect.

For some DNA analysis, the specimen must be either plucked or shed, because it must contain root or root sheath material for DNA to be extracted for further workup and identification. ‘Extraction of DNA from the biological specimen has been described by Walsh et al. (of the Roche Molecular Systems, Emeryville, CA) [93]. After extraction, two methods are used for further analysis: restriction fragment length polymorphism (RFLP) [88] and the technique, polymerase chain reaction (PCR). The RFLP technique [88] was the first one developed and provided a very high discriminating power because it discriminates by size and the number of the fragment lengths of the DNA sample. However, it cannot be used with highly degraded DNA and requires much more DNA material than the PCR technique, generally more than is provided by a single hair fiber. So, primarily because of much higher sensitivity, the PCR method has replaced the RFLP method [96].

The PCR technique offers many advantages because it requires minimal amounts of DNA and even permits typing from degraded DNA. It can even be used on single hairs as shown by Higuchi et al. [90]. PCR analysis even permits DNA analysis over a large area of the hair shaft itself. For example, Heywood et al. [97] have shown that PCR amplification permits DNA to be found even in root end and tip ends of hair, although there are higher levels in the root end. These same scientists also found that hair treated with permanent hair colorants provide lower levels of DNA and surfactant washing also decreases DNA.

After extraction, the PCR technique is used to replicate specific sections of a strand of DNA to increase the amount of material for analysis. (For further information, see bulletins describing the Gene Amp Polymerase Chain reaction Technology and the AmpliType HLA DQα Forensic Typing Kit available from the Cetus Corporation, Emeryville, CA).

Budowle and van Daal [96] describe that the discrimination power of current PCR analysis has been increased by amplifying the typing of variable number of tandem repeat (VNTR) loci. The allele forms are then separated by electrophoresis and detected by silver staining [97]. Part of a subclass of the VNTR loci has replaced the earlier markers. These new markers or short tandem repeats (STRs) are now used worldwide [98–101]. Because the fragment length of the required DNA is much smaller than in the past (about less than 350 base pairs) some degraded samples are now capable of being typed. The analysis used today is sometimes called multiplex autosomal STR loci [101]. This procedure provides high sensitivity, specificity and the capability to analyze small and degraded samples in a semi-automated manner.

Even newer techniques are under development to permit quantitation and even faster and more convenient qualitative identification of DNA for forensic, archaeological, and clinical research [79, 80].

Another type of genetic marker that shows promise for typing degraded samples involves SNPs. SNPs are single nucleotide polymorphisms or a portion of DNA where one nucleotide base has been changed, inserted or deleted. It is not likely that SNPs will ever become the primary forensic markers but they show promise to provide useful forensic information especially on degraded samples. For additional information on SNPs in forensic research see the review paper by Budowle and van Daal [96] and the sections in this Chapter entitled *Evolution of Scalp Hair to Coiled and Straight Hair Forms* and *Hair Pigmentation and Genetics*.

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Chapter 4
Reducing Human Hair Including Permanent Waving and Straightening

Abstract The physical chemistry of the primary reactions involved in permanent waving and reductive and alkaline straightening and depilation of human hair are described in detail focusing on the disulfide bond its reduction/degradation, neutralization and subsequent reactions. The influence of mercaptan structure, excess reactant, pH and cysteine in different parts of the fiber on the chemical equilibrium in this reaction is explained. Factors affecting the kinetics of this reaction such as mercaptan structure, temperature, different hair types, hair swelling and hair condition, counterion effects, other reducing agents such as sulfite or bisulfite and side reactions of the reduction process are also described. The chemistry of alkaline straightening is contrasted to permanent waving including the importance of supercontraction to its permanence. Discussion of water setting, set and supercontraction and the swelling of hair (primarily transverse changes in the fiber) at different stages of these processes are also considered. The current understanding of chemical changes to the different morphological regions of hair, the cuticle, the cell membrane complex and the cortex of hair produced by these reactions is also described.

4.1 Introduction

Significant additions to our understanding of chemical changes to the cuticle, the cell membranes, and the cortex produced by permanent waves have been added to this Chapter. In addition, thermal reconditioning or Japanese hair straightening which has been used in beauty salons has been added. Furthermore, the section on hair straightening has been expanded to include more on the mechanism of several different straightening methods and papers dealing with damage to hair by straighteners.

The primary reactions involved in permanent waving, reductive and alkaline straightening products and depilation of human hair begin with reduction or cleavage of the disulfide bond. In permanent waving and reductive hair straightening, reduced hair is stressed, i.e., curled or combed straight, while molecular

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reorganization occurs somehow involving the intermediate filaments through a disulfide-mercaptan interchange process. Neutralization is then achieved either through mild oxidation or treatment with alkali (for some sulfite treatments).

Since reduction of the disulfide bond and its subsequent reactions are vital to several important cosmetic products, a large amount of research has been conducted that is relevant to those processes. This chapter is concerned with reducing the disulfide bond in hair by mercaptans, sulfites, alkalies and other reducing agents. Reactions of reduced hair are also considered, followed by a discussion of water setting, set and supercontraction, and swelling of hair, followed by an expanded section on hair straighteners, depilatories and concluding with a section on safety of these products.

In spite of the fact that research on permanent waving has decreased over the past several decades, significant findings have been made in this field within the past three decades. For example, Wortmann and Kure [1, 2] have developed a model and extended it to show that the bending stiffness of reduced and oxidized fibers controls the permanent waving behavior of human hair and that the cuticle plays a role in permanent waving. Further, these authors have shown that the cuticle functions not only as a barrier to reduction but its stiffness also contributes to fiber set. In addition, Wortmann and Souren [3] have suggested that reorganization in the intermediate filaments is important to a permanent wave set. Our understanding of hair straightening has been expanded showing that supercontraction is essential to permanent hair straightening.

Work on fracturing reduced and oxidized-reduced keratin fibers at Textile Research Institute-Princeton provides some useful insights into damage by these reactions and a promising new test is offered to study damage to the cell membrane complex by reductive and oxidative systems. The permanent-waving process is considered in detail in this chapter including the model by Wortmann and Kure and a second useful model by Feughelman [4] followed by several cold wave compositions and procedures for making these same products in the laboratory. In addition several micrographs are included illustrating damage by reducing agents to the proteins of hair including the cell membrane complex and how these actions lead to the interesting phenomenon of scale lifting. The last section of this chapter as in previous editions describes literature relevant to the safety of reducing agents and permanent-wave products.

4.2 Reduction of the Disulfide Bond

4.2.1 Equilibrium Constants, Redox Potentials, and pH

Experiments relating to equilibrium reactions of disulfides with mercaptans commonly use reaction times of up to 24 h or longer. Although this may seem unrealistic to those in product development, extremely valuable information with practical implications has been gained from these studies.

The cleavage of the disulfide bond in keratin fibers (I) by mercaptans (II) is a reversible equilibrium reaction summarized by Equation A, where the K substituent represents hair keratin.

$$\underset{\text{(I)}}{\text{K-S-S-K}} + 2\,\underset{\text{(II)}}{\text{R-SH}} \overset{K_A}{\rightleftharpoons} \underset{\text{(III)}}{\text{R-S-S-R}} + 2\,\underset{\text{(IV)}}{\text{K-SH}} \qquad \text{(A)}$$

This reaction actually proceeds through two steps, each a nucleophilic displacement reaction by mercaptide ion on the symmetrical disulfide of hair (I in Equations A and B), and then on the mixed disulfide of hair (V in Equation C).

$$\underset{\text{(I)}}{\text{K-S-S-K}} + \text{R-SH} \overset{K_B}{\rightleftharpoons} \text{K-S-S-R} + \text{K-SH} \qquad \text{(B)}$$

$$\underset{\text{(V)}}{\text{K-S-S-R}} + \text{R-SH} \overset{K_C}{\rightleftharpoons} \text{R-S-S-R} + \text{K-SH} \qquad \text{(C)}$$

In considering these disulfide scission reactions, the equilibrium constant of the reaction shown in Equation A tells to what extent the total process will go to completion.

$$\text{Equilibrium constant} = K_A = \frac{(\text{R-S-S-R})(\text{K-SH})^2}{(\text{K-S-S-K})(\text{R-SH})^2}$$

Among the ways to determine or approximate the equilibrium constant of this type of reaction are:

1. Analysis of ingredient concentrations at equilibrium, and
2. From redox potentials [5, 6].

In either case, one may use cystine as a model for hair, since the literature [5–7] shows that the redox potential of "cystine-type" disulfides is virtually independent of the charge group about the disulfide bond. However, reduction potentials of mercaptans do vary with pH [6]. Therefore, equilibrium constants for these reactions will also vary with pH. Patterson et al. [8] have shown that when wool fiber is reacted with 0.2 M thioglycolic acid solution for 20 h the extent of reduction increases with increasing pH above 6. Assuming equilibrium, this suggests that the difference in redox potential between thioglycolic acid and cysteine in keratin fibers increases with increasing pH above 6, and the equilibrium constant for this reaction increases similarly.

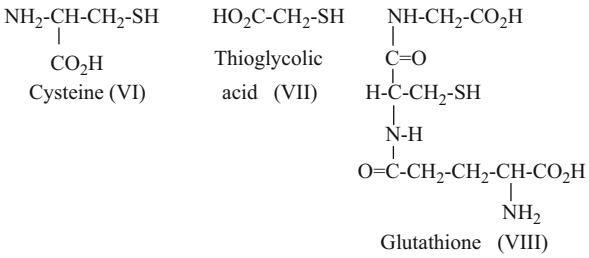
One may approximate the free energies and equilibrium constants of these reactions from these expressions:

$$\Delta F^\circ = -nfE^\circ \text{ and } \Delta F^\circ = -RT \ln K_{eq}$$

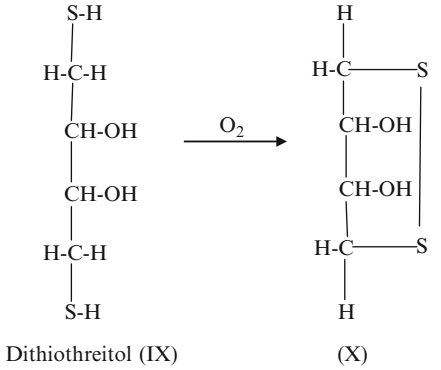
The number of electrons transferred during the reaction (2) is designated by n; f is Faraday's constant (23,061 calories per volt equivalent); E^o is the difference in standard redox potentials of the two mercaptans in volts; F^o is the standard free energy; R is the gas constant (1.987 calories per degree mole); and T the absolute temperature (°K). These calculations assume standard conditions; i.e., products and reactants are at unit activity.

4.2.2 Equilibrium Constants and Chemical Structure

Equilibrium constants at pH 7 or lower, for the reduction of cystine by simple mercaptans such as cysteine (VI), thioglycolic acid (VII), or even more complex mercaptans such as glutathione (VIII), are all approximately 1 [5, 6].



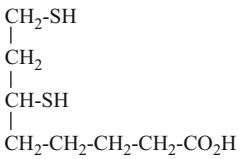
Fruton and Clark [5] have shown that the redox potentials of other cysteine-type mercaptans are very similar at pH 7.15. However, Cleland [5] has shown that dithiothreitol (IX) and its isomer, dithioerythritol, have much lower redox potentials than cysteine at neutral pH.



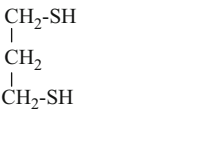
Weigmann and Rebenfeld [9] have reacted IX with wool fiber, showing that complete reduction of cystinyl residues can be approached at pH 6 to 6.5 using only a fourfold excess of IX to keratin disulfide. Cleland suggests that the equilibrium constant K_B in Equation B (of dithiothreitol and cystine) should be close to l.

However, the cyclization of IX to a stable six membered ring disulfide (X), during the reaction described in Equation C, provides an equilibrium constant of the order of $10^4 = K_C$, and therefore $K_B \times K_C = K_A$ is of the order of 10^4.

Wickett and Barman [10–12] have expanded this area of research through a series of studies that involve reduction of hair fibers under stress using, dihydrolipoic acid (XI), and 1,3-dithiopropanol (XII) which are analogs of dithiothreitol. This study demonstrated that monothio analogs of dihydrolipoic acid reduce hair at a slower rate than the corresponding dithio compounds. This correlates with the higher equilibrium constant of reaction of dihydrolipoic acid vs. cysteine. The dithio compounds can cyclize to form stable five-membered ring disulfide structures during reduction (analogous to dithiothreitol), but the monothio compounds cannot. This confirms that cyclization to stable ring structures during the reduction step can be an important driving force in this reaction.



Dihydrolipoic acid (XI)



1,3 Dithiopropanol (XII)

Wickett and Barman have further demonstrated that these five- and six-membered ring-forming reducing agents penetrate into hair via a moving boundary. This suggests nearly complete reduction as the thiol penetrates into the hair. Wickett and Barman have also demonstrated that thioglycolic acid below pH 9 does not exhibit moving boundary kinetics, but above pH 10 it does (see the section on kinetics in this Chapter). These scientists also studied structure-activity relationships of a variety of analogs of these three cyclizing dithiols illustrating the effects of hydroxyl groups and alkyl chain groupings on the rate of this reaction.

One purpose of these studies was to try to achieve essentially complete reduction of a smaller cross section of the fiber to determine if effective permanent-waving could still be achieved. A potential advantage to this type of process is to lessen cortical reduction and thereby to lessen cortical damage to the hair (the region primarily responsible for tensile properties) during the permanent-wave process.

Complete reduction in the annulus or outer regions of the hair does not occur with thioglycolic acid in current home permanent-wave products. To achieve a permanent wave, thioglycolic acid provides more diffuse reduction over a greater area of the fiber cross section [11]. This concept and its execution provide some interesting implications to the mechanism of permanent waving, suggesting that permanent set retention is not governed solely by the cortex and cannot be explained by considering only matrix reduction and consequent matrix-microfibril (matrix-intermediate filament) interactions. Moreover, strong cuticle interactions involving reduction and reshaping of the exocuticle and its A layer are probably relevant to permanent waving, and these cuticle changes should be considered in

any explanation of the permanent-wave process, as suggested and demonstrated by Wortmann and Kure [1, 2].

These ring-forming reducing agents have never been successfully introduced into the marketplace, primarily because they are sensitizing agents. Another possible concern must be greater cuticle damage by this type of action. It is conceivable that the effects of these extensive cuticle changes (essentially complete reduction of disulfide bonds in the exocuticle and A layer) on other hair properties and on long-term damaging effects from normal grooming operations could be prohibitive.

Further consideration of this two-step equilibrium process (Equations B and C) suggests the possibility for approaching complete fission of keratin cystinyl residues while producing only about 50% of the possible cysteinyl residues through formation of an extremely stable mixed disulfide (V). This type of reaction could be described as one with an extremely high K_B and a K_C of much less than 1. Haefele and Broge [13] have suggested that thioglycolamide (XIII) is such a mercaptan, on the basis of its ability to produce excellent waving characteristics in addition to excellent wet strength. No further supporting evidence has been offered to confirm this conclusion.

NH_2-CO-CH_2-SH

Thioglycolamide (XIII)

4.2.3 Equilibrium and Removal of One of the Reaction Products

O'Donnell [14] has shown that wool fiber, when reacted with thoglycolic acid at pH 5.6 approaches complete reduction of keratin disulfide by removing cysteinyl residues (IV) by means of alkylation followed by re-treatment with thioglycolic acid.

4.2.4 Equilibrium and Use of Excess Reactant

Leach and O'Donnell [15] have shown that the complete reduction of wool fiber with thioglycolic acid can be approached at pH 6.9 by employing extremely large concentrations of mercaptan (II) relative to keratin cystine (I). Similar results have been reported by Thompson and O'Donnell [16] for the reduction of wool fiber with mercaptoethanol.

4.2.5 Cystinyl Residues of Different Reactivities in Keratin Fibers

Since human hair is a complex substrate consisting of different morphological regions composed of different proteins (see Chap. 2), finding different reactivities for the same functional group is not surprising. Evidence for disulfide bonds of differing "reactivities" has been described by Middlebrook and Phillips [17] and by Carter et al. [18]. Different reactivities could be due to varying accessibilities or to differences in the electronic nature of certain disulfide bonds in the fibers resulting from differing adjacent amino acids [19]. This latter suggestion, based on work with pure disulfides and not with fibers, is contrary to the findings of Fruton and Clark [6] and to the opinion of this author. Differences are more likely to occur in reaction rate from differing accessibilities but not differences in the true equilibrium nature of the keratin disulfide reduction reaction from inductive effects.

The variation of equilibrium constant with structure, as a function of pH, has not been thoroughly explored. However, discussion of the behavior of keratin cystine in the presence of thioglycolic acid at different pH's is described in the first section of this Chapter.

Since this reduction process is a reversible equilibrium reaction, removal of one of the products of reaction (either III or IV), or use of higher concentrations of mercaptan (II) than disulfide (I), should drive the reaction to completion. Both of these principles have been confirmed.

4.3 Kinetics of the Reduction

All cleavages of simple disulfides by mercaptans that have been studied kinetically are bimolecular ionic reactions of the SN 2 type, involving direct displacement by mercaptide ion on disulfide as described by Foss [20] and most Organic Chemistry textbooks. Since the active species in this disulfide scission process is the mercaptide ion [21] rather than the unionized mercaptan, pH is a critical factor. As a consequence, pH can determine the rate-controlling step in the reductive cleavage of cystinyl residues in keratin fibers by mercaptans. For example, in the reaction of wool fiber with dithiothreitol, Weigmann [22] has shown that the rate-controlling step at pH 7.0 and above is diffusion of the reducing species into the fibers. However, at acidic pH (3.5), the chemical reaction itself appears to be rate-limiting. A similar change in mechanism with pH has been suggested by Kubu and Montgomery [23] for the reduction of wool fiber by cysteine and also for the reduction of human hair by several thiols, including thioglycolic acid [24].

Wickett [10] has shown that for the reaction of sodium thioglycolate with one lot of hair, at pH 9 or below, the rate of the reaction followed pseudo-first-order kinetics and therefore was reaction-controlled. However, at pH 10 and above,

moving boundary kinetics or diffusion of mercaptan into the hair controlled the reaction rate. Wickett further demonstrated under conditions closer to those of actual permanent waving (pH 9.5 and 0.6 M sodium thioglycolate) that for hair from one individual who exhibited high reactivity, the reaction rate followed pseudo first order kinetics. For hair from another individual, which was more difficult to wave, diffusion of the reducing agent into the hair was the rate-determining step. Thus for difficult-to-wave hair, the rate of the reaction of thioglycolate waves is governed by diffusion of the reducing agent into the hair.

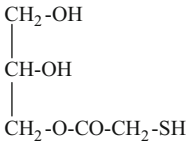
In other words, for difficult-to-wave hair or at high pH, the concentration of mercaptide ion is so high that cleavage of the disulfide bond can occur faster than mercaptide can diffuse into the fibers. As the pH is decreased to the acid side, or for easy-to-wave hair, the rate of chemical reaction decreases faster than diffusion to the point at which the chemical reaction itself becomes rate limiting. With many mercaptans [21], further lowering of the pH to about two freezes or stops the reduction reaction.

Evans et al. [25] have confirmed these conclusions of Wickett. In addition, the observation that Japanese hair is "easy to perm" and that fine Caucasian hair, less than 75 μm in diameter, is more "difficult to perm" was also confirmed. However, these scientists were unable to identify any common characteristics such as fiber diameter or cystine content that would account for this behavior. The fact that fine hair is more difficult to perm than thick hair may be due to the larger ratio of cuticle to cortex in fine hair and the fact that cortex plays a stronger role in waving than cuticle. This explanation is consistent with the experiments by Wortmann and Kure [2] demonstrating that the cuticle does inhibit the reduction reaction. In addition to pH, other important variables that influence the rate of reduction of keratin fibers by mercaptans are temperature, hair swelling, prior history of the hair, and structure of the mercaptan. These factors are described in the next section of this Chapter.

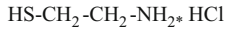
4.3.1 Factors Affecting the Rate of the Reduction Reaction

Since the rate-controlling step in this reaction can be diffusion of the reducing agent into the fibers or the chemical reaction itself, it is important to consider the rate in terms of these two potentially rate limiting factors.

The pH region most commonly employed for the reduction of hair fibers by mercaptans is above neutral (generally 9–9.5). In the professional field, glyceryl-monothioglycolate (GMT) was introduced in Europe in the 1960s and into the U.S. in the 1970s [24, 26]. This thiol is the active ingredient used in several commercial acid waves where the waving solution has a pH near 7. It would appear that the reaction of GMT with hair is a reaction-controlled rate process, since the pH of the system is near 7.



Glycerylmonothioglycolate (GMT)



Cysteamine Hydrochloride

The processing time for a GMT permanent is about twice as long as for a conventional thioglycolate wave and it requires a covering cap and the heat of a dryer to enhance the rate of reduction. Wickett [10] has shown that for sodium thioglycolate under conditions where reaction rate control exists, the activation energy is lower than for diffusion rate control. Therefore, under these conditions an increase in temperature will have less of an effect on the reaction rate than if the reaction were a diffusion-controlled process. The acid wave supporters claim superiority due to reduced swelling and less damage; however, no data could be found to support these claims. To date, GMT acid waves have been used only by professionals and not in the retail field [26].

Cysteamine hydrochloride is another active thiol used in professional products at a lower pH about 8.3. Manuszak et al. [27] have compared the reduction of hair by cysteamine and thioglycolic acid. At a pH where similar concentrations of mercaptide ion were present, thioglycolic acid was more effective in reducing the fibers. One explanation is that cysteamine forms an internal five membered ring structure via internal hydrogen bonding from the protonated amine group to the mercaptide group, thereby reducing its availability for reaction.

4.3.2 Effect of Temperature on the Reaction Rate

The activation energy for the reduction of either human hair or wool fiber at alkaline pH is of the order of 12–28 kcal per degree mole [10, 22, 24]. Wickett [10] explains that when the mechanism is diffusion-rate-controlled, the activation energy is higher (28.0 kcal per degree mole) [10], because the boundary movement depends on both reaction and diffusion. However, when the rate depends only on the chemical reaction, the activation energy is lower (about 19.7 kcal per degree mole). Therefore, reaction rates for both of these systems are only moderately affected by increases in temperature. The activation energy for the chemical reaction at acid pH is slightly lower [22]. Therefore, the rate of reaction under acid conditions should be affected less by changes in temperature.

Japanese hair straightening a process that involves reducing the hair and then applying a hot straightening iron to it to achieve a permanent straightening hair treatment will be described later in this Chapter in Sect. 4.12.

4.3.3 *Effect of Hair Swelling and Hair Condition on the Reaction Rate*

Above the isoelectric point, the swelling of hair increases substantially with increasing pH [28, 29] (also see Chap. 9). Herrmann [24] has shown a corresponding increase in the rate of diffusion of mercaptans into hair fibers with increasing pH. Hydrogen bond breaking agents (hair swelling agents), namely urea and other amides, have been added to depilatory formulations for the purpose of enhancing the rate of reduction [24, 29]. Heilingotter [30] has shown that the addition of urea to thioglycolic acid solution increases the rate of swelling of the fibers. Depilatory systems are generally high-pH mercaptan systems (pH 11 to 12) where moving boundary kinetics exists under all conditions [10], and a common depilatory ingredient is calcium thioglycolate (see Fig. 4.1 and the section on depilatories in this Chapter). Note the axial folds created by the extreme swelling and then rapid dehydration on drying. These folds are created because of the differential shrinkage in the different cuticle layers due to extensive bond breaking and the leaching out of solubilized proteinaceous matter.

Undoubtedly, the condition of the hair also plays a role in the rate of reduction, especially under conditions where diffusion is rate-limiting. Permanent-waving [31] and bleaching [32] produce alterations to hair that result in increased swelling in solvents. Also, hair that has been previously bleached or permanent-waved displays more rapid rates of reduction than chemically unaltered fibers. As a consequence, weaker reducing systems are offered in the marketplace to permanent-wave

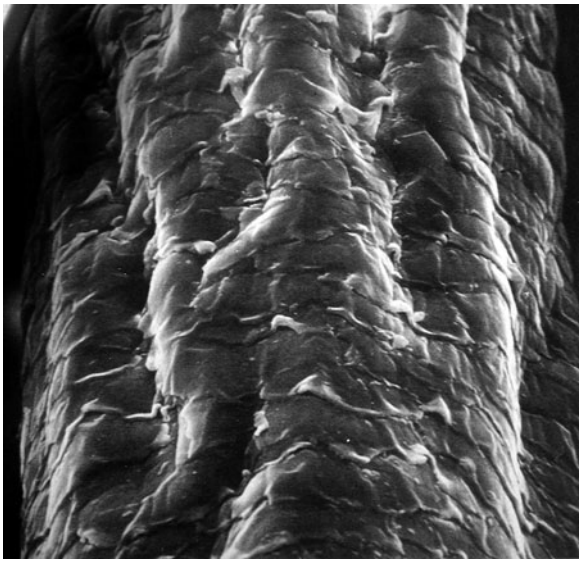


Fig. 4.1 Hair fiber after treatment with calcium thioglycolate (depilatory)

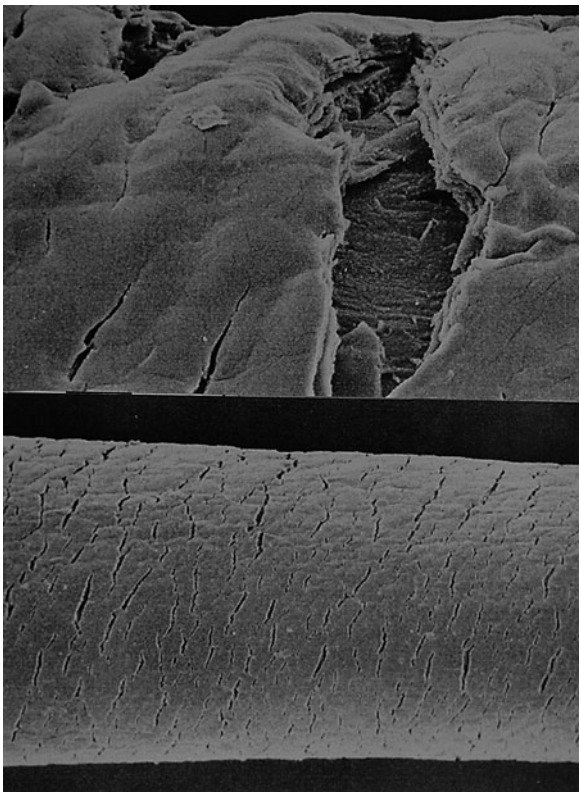


Fig. 4.2 Hair fiber oxidized with peroxide, reduced with thioglycolate and extended to fracture dry. *Bottom*: At low magnification, note the cracks perpendicular to the fiber axis. *Top*: Higher magnification shows cracks are through the entire cuticle (SEM kindly provided by Sigrid Ruetsch)

hair that has been previously damaged by bleaches and other damaging chemical treatments.

Figures 4.2 and 4.3 illustrate the large amount of damage inflicted on hair fibers by combined oxidation and reduction treatments. These fibers were oxidized with alkaline peroxide and then reduced and extended to fracture in the dry state. All of the fibers treated in this manner broke between only 10% and 20% extension as opposed to fibers that had been only reduced. The reduced fibers broke at a significantly higher extension. Figure 4.2 illustrates the large number of deep cracks in the cuticle perpendicular to the fiber axis that extend through all the cuticle layers. The SEM of Fig. 4.3 was taken at the fracture site itself and shows multiple step fractures and even torn cuticle and cortical cells resulting from extensive damage to the proteins of the cell membrane complex and to proteins in both cuticle and cortical cells. Although these treatments are stronger than generally used in practice, they illustrate the greater sensitivity of bleached hair to reductive treatments and also just how degrading combined bleaching and permanent waving can be.

An initiation time for the reduction reaction was found by Weigmann [22] in his kinetic study of the reduction of wool fiber. Weigmann attributed the initiation time

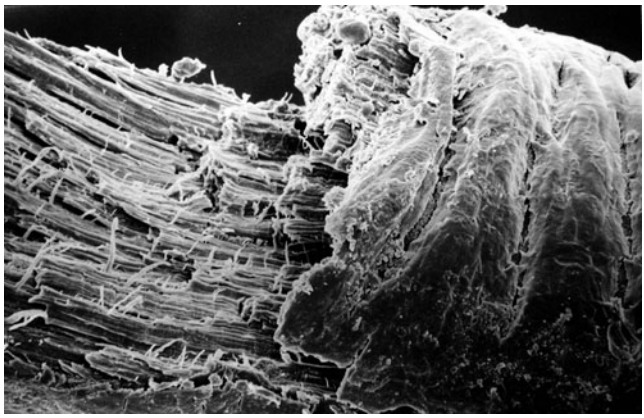


Fig. 4.3 Fiber was oxidized, reduced and extended to break dry. This SEM was taken at the fracture site. Note the multiple step fractures in the cell membrane complex (SEM kindly provided by Sigrid Ruetsch)

to the epicuticle the initial barrier to reduction that is eliminated after a short reduction time. It is likely that the initial reduction reaction cleaves some thioester linkages removing some 18-methyl eicosanoic acid from the surface but it would appear that the major breakdown in the cell membranes by permanent waves involves the cleavage of disulfide bonds by the thiol active in the permanent wave which weakens the membranes and leaves a high concentration of mercaptan groups to allow further membrane degradation under stress and in that manner the diffusion barrier of the hair surface is degraded. As a consequence, hair that has been permanent-waved or has undergone alterations to its outer layers should provide less or no initiation time in subsequent reductions or reactions.

Diffusion rates are significantly greater in wool fiber than in human hair [33]. This effect is due to the lower disulfide content of wool fiber relative to human hair. Therefore, one might anticipate a more rapid rate of reduction for wool fiber than for human hair, under conditions of diffusion-controlled reduction.

Scale lifting by alternating treatments of certain anionic and cationic surfactants can occur on hair previously permanent waved or extensively bleached, see Figs. 4.4 and 4.5. Furthermore, hair purchased from consumers who had been given a home or salon permanent wave on the head shows an even greater propensity for this type of scale damage than hair permed in the laboratory. We believe that this phenomenon involves scale lifting through a weakened cell membrane complex. Figure 4.6 depicts the damaging effects of reductive treatments on the cell membrane complex. This fiber was reduced and not re-oxidized chemically and then extended to break. Note the large gaps between cuticle cells and at the cuticle-cortex junction created by the weakened cell membrane complex. Such gaps do not occur in the cell membrane complex by extending chemically unaltered hair to break. This reaction likely involves cleavage of thioester in the surface and in each layer between cuticle cells by thiolate of the TGA because

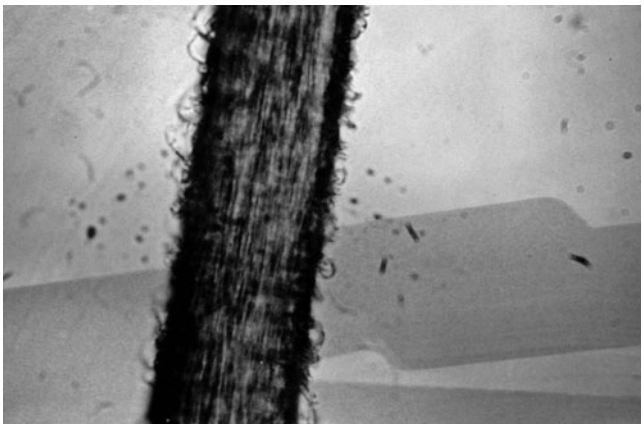


Fig. 4.4 Fiber was permanent waved on the head, after a few weeks cut, and treated with three alternating treatments of TEA lauryl sulfate and stearalkonium chloride and observed in the light microscope. Note the lifted cuticle scales

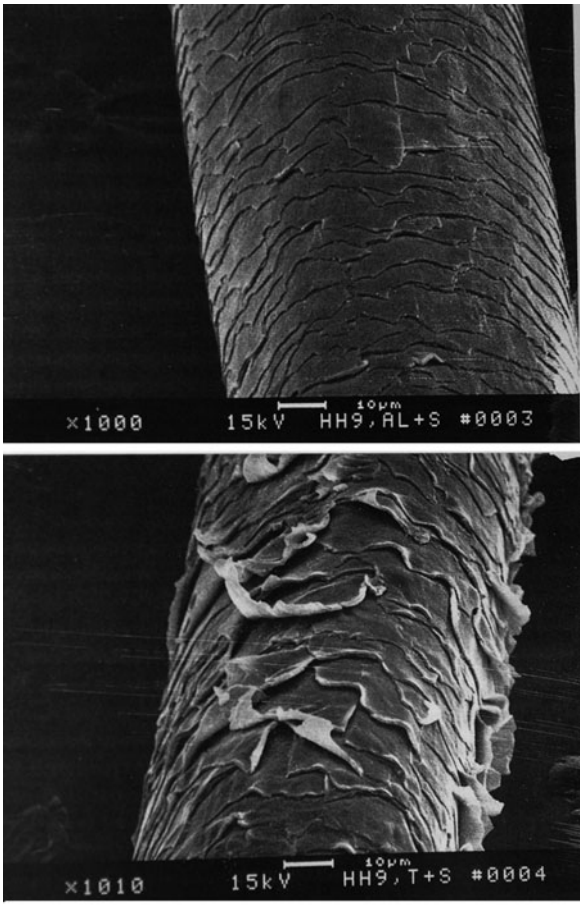


Fig. 4.5 Similar treatment as in Fig. 4.4, except this fiber was observed in the dry state by SEM. *Top*: Control treated with sodium deceth-3 sulfate and stearalkonium chloride. *Bottom*: Treated with TEA lauryl sulfate and stearalkonium chloride. Note the lifting of scales due to the weakened cell membrane complex

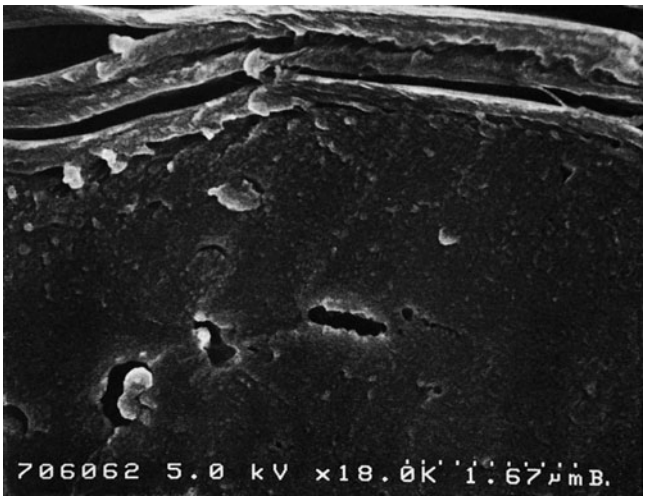


Fig. 4.6 Fiber reduced with TGA at pH 10 and extended to break dry. Note the cracks between the scales caused by a weakened CMC (SEM kindly provided by Sigrid Ruetsch)

thioester is sensitive to nucleophiles and the thiol grouping is one of the most powerful nucleophiles in organic chemistry.

The scale lifting phenomenon described above is due primarily to the penetration of cationic and anionic surfactant into the endocuticle and the cell membrane complex and the subsequent deposition and build-up of a hydrophobic anionic-cationic complex layer. When this layer is sufficiently large, a lifting action is created by the differential swelling action in the cuticle layers. This effect is analogous to the bending action of a laminar thermostat to heat changes. The fact that hair permed on heads is more reactive to this scale lifting phenomenon suggests greater cell membrane complex damage on live heads compared to laboratory waving. I believe this effect is due to weathering exposures on permanent waved hair such as "fatiguing like actions" during grooming that result primarily from combing and brushing actions or other damaging exposures such as UV radiation. This scale lifting phenomenon could provide a simple test to detect and define the extent of damage to the cell membrane complex. For a more complete description of this scale lifting phenomenon, see Chap. 6.

Figure 4.7 also represents hair fibers reduced and then extended to fracture and shows effects occurring deeper inside the fiber. The fracturing of this fiber clearly shows that reductive treatments do weaken the cell membrane complex extending across the entire fiber even into the medulla. This electron micrograph provides an interesting view of the structure of the medulla confirming that it consists of hollow spheres rather than simply a porous region of the fiber.

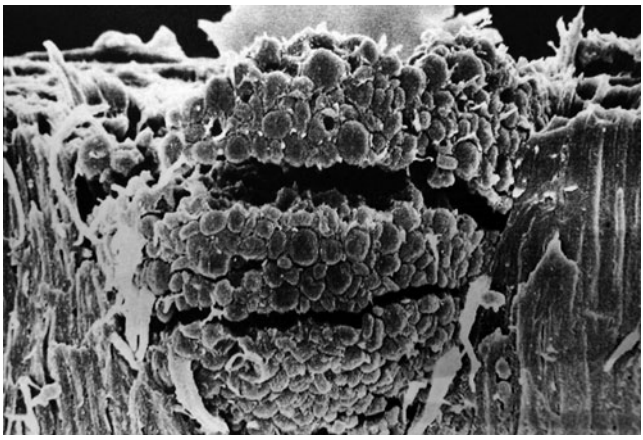


Fig. 4.7 Fiber reduced and extended to fracture dry. The medullary cracks show that reductive treatments weaken the intercellular structures of the entire fiber, even in the medulla (SEM kindly provided by Sigrid Ruetsch)

4.3.4 Effect of Mercaptan Structure on the Reaction Rate

4.3.4.1 Electrostatic Effects

Herrmann [24] described a minimum at acid pH for the diffusion of a cationic containing thiol (thioglycolhydrazide) into human hair. He also examined the influence of pH on the

$$HS\text{-}CH_2\text{-}CO\text{-}NH\text{-}NH_2$$

Thioglycolhydrazide

rate of diffusion of thio acids (thioglycolic and thiolactic acids) into human hair. For this latter type of mercaptan, the minimum in diffusion rate occurs near neutral pH. These thio acids are of anionic character in alkaline media, and they diffuse faster in alkaline than in acidic media. Therefore, hair swelling must play a more important role than electrostatics for the diffusion of these simple mercaptans into human hair.

4.3.4.2 Nucleophilicity of the Mercapto Group

The nucleophilicity of the mercaptan grouping depends on the nature of the groups directly attached or in close proximity to the mercaptan functional group. In general, nucleophilicity increases with increasing basicity of the mercaptan function [34]. Over the range of conditions where diffusion is rate-limiting, changes to the nucleophilicity of the mercapto group will have little effect on the rate of reduction. However, where the chemical reaction is rate-controlling, the

nucleophilicity of the mercapto group will be of greater importance. Theoretically, in a diffusion-controlled reduction, one could increase the rate of reduction by sacrificing nucleophilicity (decrease the basicity of the mercaptide ion) in order to increase diffusibility.

Haefele and Broge [35] have reported the mercapto acidities for a large number of mercaptans (pK RSH 4.3 to 10.2); thioglycolic acid is just above 10 (10.4). Hydrogen sulfide, the simplest mercaptan, has a pK RSH of 7.0 [35]. As one might predict, the substitution of electron-withdrawing groups (carbonyl, alkyl ester, alkyl amide) for a hydrogen atom increases the mercapto acidity. Electron- donating groups (carboxy, alkyl) decrease mercaptan acidity.

Under conditions of lower pH, where this reduction process is reaction-controlled rather than diffusion-controlled, Equation B or C can be rate-limiting. If Equation B is rate-limiting, the reaction is simply second order—first-order with respect to mercaptan and first-order with respect to keratin disulfide—and analysis is not as complicated as when Equation C is rate-limiting. In kinetic studies for a complex material like human hair or wool fiber, an excess of thiol is most commonly employed, and one generally assumes the reaction in Equation B to be rate-controlling. The reaction is then described by pseudo-first-order kinetics (first-order with respect to keratin disulfide).

4.3.4.3 Steric Effects

The rate of diffusion of mercaptans into human hair is undoubtedly influenced by steric considerations. For example, molecular size (effective minimum molecular diameter) of the mercaptan molecule should affect the rate of diffusion into hair. Therefore, the rate of reduction of human hair by ethyl mercaptan in neutral to alkaline media, where diffusion is rate-determining, should be faster than that of higher homologs. (The possible effects produced by varying the structure of cystinyl residues in hair on the rate of reduction were considered in the previous section on cystinyl residues of differing reactivities.)

4.3.4.4 Counterion Effects

Ammonia or alkanolamines such as monoethanol amine are the primary neutralizing bases for reducing solutions of thioglycolate permanent waves. Ammonia is said to facilitate diffusion of thioglycolate through hair as compared to sodium hydroxide [36].

Heilingotter [37, 38] has compared a large number of neutralizing bases including ammonia, monoethanol amine, sodium hydroxide, isopropanol amine, ethylene diamine, diethanol amine, and triethanol amine with regard to the ability of the corresponding salts of thioglycolic acid to decrease the 20% index (at a pH close to 9.2). This criterion was used to assess the ability of these different thioglycolates to function as permanent-wave reducing agents. He found that ammonia and

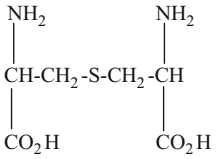
monoethanol amine provide the maximum effects. Furthermore, the reducing power of triethanolamine thioglycolate is so weak as to render it ineffective as a permanent-waving agent.

Heilingotter suggested that of the two most effective reducing systems, ammonium thioglycolate provides the more satisfactory waving characteristics. It would appear that this "catalytic activity" of nitrogen-containing bases is due to their ability to swell the hair, thus allowing faster diffusion of mercaptan into the interior of the fiber.

Other salts of thioglycolic acid have been described as potential permanent-waving agents, including potassium [39], magnesium [40] and of course esters such as glycerol monothioglycolate and other esters [41]. Magnesium thioglycolate has been described as an odorless permanent wave agent, although this system has never achieved commercial success.

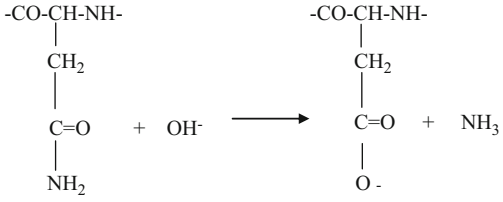
4.3.4.5 Side Reactions During the Reduction of Keratin Fibers with Mercaptans

The reaction of mercaptans with keratin fibers is a relatively specific reaction in mild acid. However, in alkaline media, peptide bond hydrolysis and the formation of lanthionyl residues can also occur [42]. Zahn et al. [43] suggested that mercaptides such as thioglycolate or cysteinate can accelerate the rate of formation of lanthionyl residues in wool fiber. (A more detailed discussion of the formation of lanthionyl residues in keratin fibers is described later in this Chapter.)



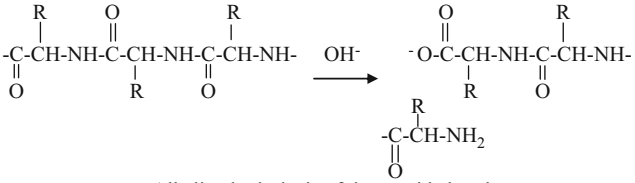
Lanthionine

Hydrolysis of peptide and amide linkages is also a possible complication in an alkaline medium. Hydrolysis of the amide groups of the residues of aspartic and glutamic acid amides will increase the ratio of acidic to basic groups in the fibers, conceivably altering the isoelectric and/or isoionic points of the hair.



Hydrolysis of amide of aspartic acid

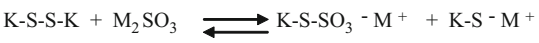
Peptide bonds are the major repeating structural unit of polypeptides and proteins, and they form the structural backbone of human hair. Hydrolysis of peptide bonds can also occur at high pH, and both of these reactions (hydrolysis of amide and peptide bonds) are far more prevalent in the action of depilatories, formulated near pH 12, than in permanent waves. Permanent-waving lotions are usually formulated at a pH of approximately 9.2–9.6.



Alkaline hydrolysis of the peptide bond

4.4 Reduction of Hair with Sulfite or Bisulfite

Sulfites or bisulfite (depending on pH) are another important reducing agent for the disulfide bonds in commercial permanent waves. The reaction of sulfite with hair involves nucleophilic attack of sulfite ion on disulfide. This reaction produces one equivalent of mercaptan and one equivalent of Bunte salt [44].



Bunte salt

Reese and Eyring [45] demonstrated that the reaction of sulfite with hair is a pseudo-first-order reaction. In other words, the chemical reaction of sulfite with the disulfide bond of hair is slower than diffusion of sulfite into hair. Elsworth and Phillips [46, 47] and Volk [48] examined the sulfitolysis of keratin, demonstrating that the rate of cystine cleavage is optimal at acid pH. Wolfram and Underwood [49] found a broad optimum for cystine cleavage by sulfite at pH 4–6. The decrease in cystine cleavage at acidic pH (below pH 4) is due to a decrease in the concentration of the nucleophilic sulfite species. On the other hand, the decrease in cystine cleavage as pH is raised (alkaline pH) results from alkaline hydrolysis of the Bunte salt [50].

The patent literature teaches that rebuilding disulfide bonds in keratin after sulfitolysis may be accomplished through water rinsing. However, reversal of sulfitolysis by rinsing is normally slow and inefficient [26]. In addition, Bunte salt is resistant to oxidizing agents. Therefore, neutralizers such as bromate or hydrogen peroxide are not totally efficient in rebuilding disulfide bonds in sulfite waves.

Sneath [51] showed that the bisulfite waving treatment decreases the barrier function of the cell membrane complex as evidenced by cationic dye absorption,

however, part of this reaction is reversible, and therefore, probably involves the Bunte salt groupings. In addition, lipids (including 18-methyl eicosanoic acid) are removed from the cell membrane complex during bisulfite waving and this part of the reaction is not reversible and a higher concentration of mercaptan and oxidized sulfur are left in the hair to weaken it.

To summarize and to compare the two processes of thioglycolate and sulfite reduction of hair, we find that the thiol (or nucleophile) reacts with hair, producing cysteine residues in the following manner:

$$\text{K-S-S-K} + 2\ \text{R-SH} \rightleftharpoons 2\ \text{K-SH} + \text{R-S-S-R}$$

This reaction can be largely but not completely reversed by rinsing and oxidation in air. However, the most effective reversal is achieved through mild chemical oxidants.

On the other hand, sulfite reacts with the disulfide bonds in hair to produce mercaptan and Bunte salt:

$$\text{K-S-S-K} + \text{SO}_3^- \rightleftharpoons \text{K-S}^- + \underbrace{\text{K-S-SO}_3^-}_{\text{Bunte salt}}$$

Rinsing of the sulfite-treated hair slowly reverses the reaction, rebuilding cystine bonds. The rate of cystine reformation increases with increasing pH, and good set stability is achieved at pH 8 or higher. Because of the efficiency of reversal of the sulfitolysis reaction with alkali, Albrecht and Wolfram [52] suggest that for low cleavage levels, sulfite is a more effective setting agent than thioglycolate. However, at higher cleavage levels, thioglycolate is the superior active ingredient.

In addition, thioglycolate at alkaline pH is more effective at higher cleavage levels, because thioglycolate is a stronger reducing agent than sulfite. Its greater effectiveness is borne out by the fact that under optimum conditions, for difficult-to-wave hair, the rate-controlling step for the thioglycolate reaction is diffusion of the reducing species into the fibers [10]. On the other hand, for sulfite at its optimum (acid pH), the rate-determining step is chemical reaction with the disulfide bond.

4.5 Summary of Chemical Changes to Hair by Permanent Waving

As hair is exposed to permanent waving, changes take place in the surface layers, the cell membrane complex, the A-Layer and exocuticle in addition to the cortex leading to the formation of increasing concentrations of these sulfur compounds, mercaptan, sulfinate and sulfonate groups and a decrease in the free lipid content in the surface layers. Zahn et al. [53] have shown an increase in the thiol content of

whole fiber from about 11 μmol/g in untreated hair to as high as 94 μmol/g for permanent waved hair and Robbins and Kelly [54] has shown similar amounts of cysteic acid in permanent waved hair actually waved on people's heads (49–94 μmol/g) vs. about 25 μmol/g for controls. Since a normal permanent wave usually reduces less than 50% of the whole fiber in cross-section these values are likely to be much higher in the outer layers of the fiber.

Kon et al. [55] examined Japanese hair permanent waved on live heads every 2–3 months comparing it to untreated controls. These scientists analyzed two types of permanent waved hair: Permed hair with many splits and permed hair with several broken hairs and a few split ends. This latter hair, by SEM analysis, showed considerably less cuticle most likely from abrasive actions such as combing and brushing. From analysis of 18-methyl eicosanoic acid and isopeptide (cuticle analyses) the following results were revealed, see Table 4.1.

The data of Table 4.1 were calculated from the results by Kon et al. [55] and show very little change in MEA from the control to the permed hair in the mid-sections compared with the tip ends. Because the thiol will not attack the isopeptide linkage and considering the fact that such large changes occur in the isopeptide content of the permed hair, these large changes suggest that greater effects are produced in this hair by abrasive actions which remove cuticle proteins and lipids than by direct chemical action of the thiol. Therefore the chemical and physical changes from permanent waving have a profound effect on reducing the abrasion resistance of hair.

With regard to effects on the cortex, Kon et al. [55] found that permanent waving produced a significant decrease in microfibril protein and an increase in high molecular weight protein which showed up most readily in the tip ends of the hair. This increase in high molecular weight protein probably results from a disulfide-mercaptan interchange reaction.

With regard to the changes most relevant to shampoos and hair conditioners, these reactions of permanent waving, convert the virgin hair surface from a hydrophobic, entity with little surface charge to a more hydrophilic, more polar and more negatively charged surface. More of the lower oxidation state sulfur compounds are formed in permanent waved hair and exist after waving as compared to chemically bleached hair or sunlight oxidized hair. These surface and

Table 4.1 18-MEA and isodipeptide in cuticle of permanent waved hair and control hair [55]

Hair/treatment	Mid-sections Δ at 10–20 cm[a]		Tip ends Δ at 30–40 cm[b]	
	IP[c]	MEA[d]	IP[c]	MEA[d]
Control	−9	−25	−18	−36
Perm (splits/more cuticle)	−27	−25	−64	−45
Perm (broken less cuticle via abrasion)	−36	−48	−82	−79

[a]Percentage change at 10–20 cm vs. control (560 μg/g at roots (0–10 cm)
[b]Percentage change at 30–40 cm vs. control (560 μg/g at roots (0–10 cm)
[c]Confidence levels from about ±25% to much higher
[d]Sensitivity = confidence levels ±10% to 15%

curvature changes produce higher rubbing forces resulting in more cuticle protein and lipid removal by hair grooming actions.

4.6 Reduction of Keratin Fibers with Other Reagents

In addition to mercaptans and sulfites, ingredients that have been used for nucleophilic cleavage of the disulfide bond in hair and/or wool fiber are sulfides, hydroxide, water (steam), a phosphine, borohydride, dithionite (hydrosulfite), and sulfoxylate. The interactions of some of these compounds with the disulfide bond in hair are described below.

4.6.1 Sulfides

Salts of hydrogen sulfide are extremely potent reducing agents for hair and have been used in depilatory compositions [56]. In a sense, salts of hydrogen sulfide are the simplest and among the most diffusible of all mercaptans. The initial reaction with the disulfide bond in keratin fibers is described by Equation D. Obviously, compound XIV can also ionize and react with cystinyl residues, forming organic polysulfides. Compound XIV can even react with hydrogen sulfide (anion) to form inorganic polysulfide.

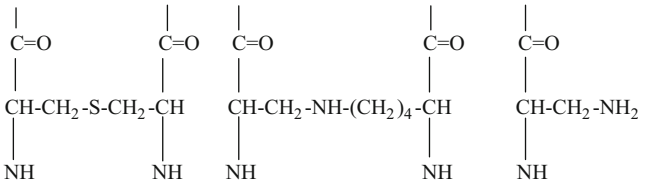
$$\text{K-S-S-K} + \text{M}^{+}\ {}^{-}\text{S-H} \rightleftharpoons \underset{\text{(XIV)}}{\text{K-S-SH}} + \text{K-S}^{-}\ {}^{+}\text{M} \qquad \text{(D)}$$

4.6.2 Steam and/or Alkali

Setting of wool and hair by either steam or hot alkaline solutions is a very old process [57]. Steam is also very effective for producing a permanent set. Alkali and steam are known to cleave the disulfide bond in keratins [58–60] and alkaline treatments are known to be the most effective hair straightening compositions because they provide the most permanent set (see the section on hair straightening in this Chapter). The reaction with hydroxide is summarized below by Equation E. Since sulfenic acids are generally unstable species [61], they have been suggested as intermediates that can react with the nucleophilic side chains in the keratin macromolecules [59].

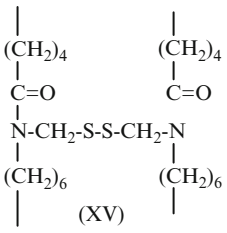
$$\text{K-S-S-K} + \text{M}^{+}\ {}^{-}\text{O-H} \rightleftharpoons \underset{\text{Sulfenic acid}}{\text{K-S-OH}} + \text{K-S}^{-}\ \text{M}^{+} \qquad \text{(E)}$$

As mentioned before, hydrolytic cleavage of peptide bonds in keratins, as well as formation of lanthionyl residues can also occur in alkali. In addition to lanthionine, lysinoalanine [62] and Beta-aminoalanine [63] residues can be formed in some keratins under alkaline conditions.



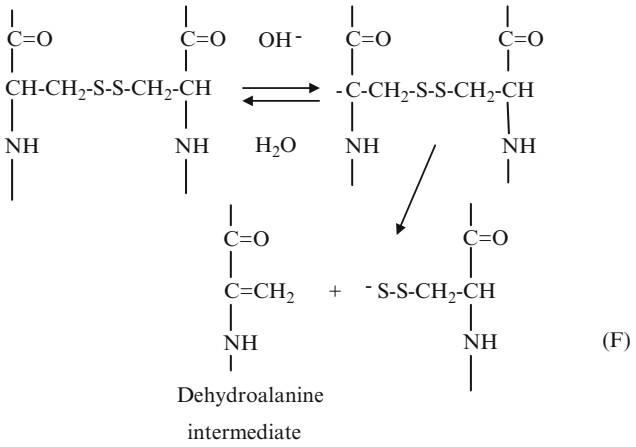
Formation of lanthionyl residues during alkaline treatment of keratin fibers was first suggested by Speakman [64] and later demonstrated by Horn et al. [65]. Lanthionyl residues may be formed from cystinyl residues in proteins under relatively mild alkaline conditions: 35°C and pH 9–14 [42]. However, under these same reaction conditions, lanthionine has not been identified from free cystine. For that matter, thioethers have not been formed from organic disulfides other than cystine-containing proteins, using similar reaction conditions [66]. At a higher reaction temperature (reflux), Swan [67] claims to have identified small quantities of lanthionine from reaction of alkali with free cystine.

Earland and Raven [68] have examined the reaction of N-(mercaptomethyl) polyhexamethyleneadipamide disulfide (XV) with alkali. Under alkaline conditions that produce lanthionyl residues in wool, no thioether is formed from this polymeric disulfide; however, cyanide readily produces thioether from both (XV) and wool fiber. Therefore, the mechanism for thioether formation must be different in these two reactions. Since this polymeric disulfide (XV) contains no betahydrogen atoms (beta to the disulfide group), a likely mechanism for formation of lanthionyl residues in keratins, under alkaline conditions, is the beta-elimination scheme [67] (the reaction depicted by Equation F). Other mechanisms that have been suggested for this reaction have been summarized by Danehy and Kreuz [69].



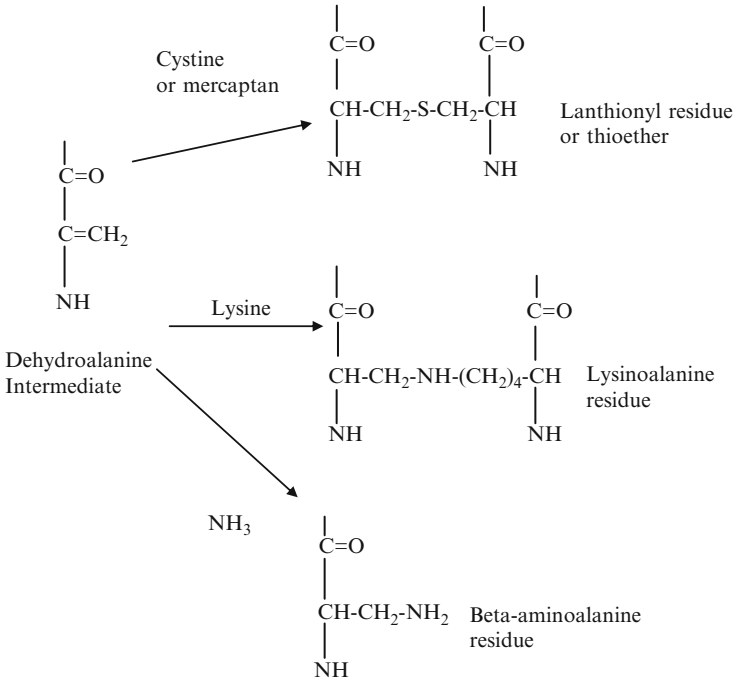
(XV)

The formation of lanthionine in keratin fibers is believed to involve two reaction sequences. The first sequence consists of beta-elimination to form dehydroalanine residues in hair:



Reaction sequence 1: beta-elimination to form dehydroalanine intermediate residue.

The disulfide anion (of reaction sequence 1) may then eliminate sulfur to form mercaptide ion. In addition, the dehydroalanine intermediate is a very reactive species. It may react with any nucleophilic species present, such as mercaptan or amine, including mercaptan or amine residues on the hair or such groups in solution, to form lanthionine (other thioethers), or lysinoalanine [66, 70, 71], or beta-aminoalanine residues [63, 70–72] as shown below.

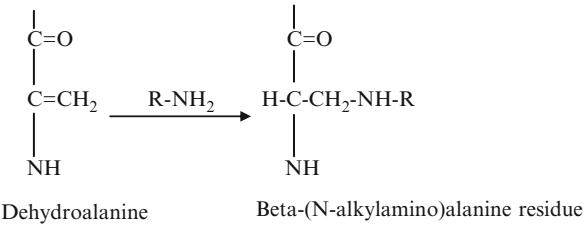


Second sequence of reactions: Nucleophilic addition to dehydroalanine

For wool fiber, all three residues-lanthionine, lysinoalanine, and beta-aminoalanine have been shown to form from reactions under alkaline conditions [70, 72, 73]. In the case of human hair, only lanthionine and lysinoalanine have been shown to form under alkaline conditions and lanthionine has been found at more than 100 micromoles per gram of hair in hair treated with 0.1 N sodium hydroxide under conditions similar to that of a hair straightener product [71], whereas no lanthionine was found in untreated control hair.

4.6.3 Amines

The discussion above on the reaction of alkalinity with wool and hair shows that a very reactive intermediate, dehydroalanine, is formed in hair and wool in the presence of alkalinity at elevated temperature (30–40°C or Chigher). Rivett [73] and Tolgyesi and Fang [71] have studied the reaction of wool and hair in the presence of alkaline amine solutions. Under these conditions, one might conclude that if amines are at a sufficient concentration they might add to the dehydroalanine intermediate to form beta-(N-alkylamino) alanine residues.



Dehydroalanine Beta-(N-alkylamino)alanine residue

Such is the case. However, the actual products formed depend on the substrate (hair vs. wool), the structure of the amine, its concentration, and the reaction temperature.

With short-chain amines like ethyl or n-butyl amine in the presence of wool fiber in alkali, the amounts of lanthionine and lysinoalanine are less (compared to alkali alone), but these two species are still produced in detectable quantities. However, longer-chain amines like pentyl amine react quantitatively with wool fiber and virtually no lanthionine or lysinoalanine is formed.

Tolgyesi and Fang [71] have found that alkaline amine solutions react differently with human hair. With human hair, all amines examined, including pentyl amine, compete less effectively with the amino and mercaptan residues of the hair for the dehydroalanine intermediate. As a result, more lanthionine and lysinoalanine cross links form than amine adduct, when human hair is the substrate. This is probably because diffusion rates are slower into human hair, decreasing the effective concentration of free amine in the fibers. Therefore, these species cannot compete as effectively for the dehydroalanine intermediate, and therefore lanthionine and lysinoalanine are formed.

4.6.4 Cyanide

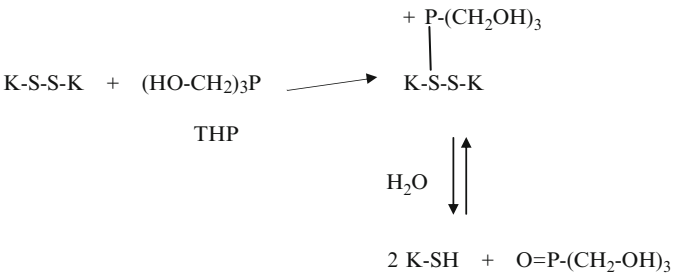
Salts of hydrogen cyanide have also been found to be capable of nucleophilic cleavage of the disulfide bond in keratin fibers [74]. In addition, nearly quantitative conversion of cystinyl residues to lanthionyl residues can be achieved in this reaction [75]. The most plausible mechanism is given in Equations G and H [65]. This mechanism consists of two nucleophilic displacement reactions: the first by cyanide on sulfur, and the second by mercaptide ion on carbon. The mechanism below is consistent with the observed formation of thioether from the reaction of N-(mercaptomethyl)polyhexamethyleneadipamide disulfide (XV) with cyanide, but not with alkali [68].

$$\text{K-S-S-K} + \text{M}^+ \ ^-\text{CN} \longrightarrow \text{K-S-CN} + \text{M}^+ \ ^-\text{S-K} \qquad \text{(G)}$$

$$\text{K-S-CN} + \text{M}^+ \ ^-\text{S-K} \longrightarrow \text{K-S-K} + \text{M}^+ \ ^-\text{S-CN} \qquad \text{(H)}$$

4.6.5 A Phosphine

Trihydroxymethyl phosphine (THP) or its precursor, tetrahydroxymethyl phosphonium chloride, has been used to reduce both human hair and wool fiber [75]. The mechanism of this reaction was studied by Jenkins and Wolfram [76], who discovered that this reaction proceeds by nucleophilic attack by the phosphine on sulfur, followed by hydrolysis of the intermediate addition compound to mercaptan and phosphine oxide.



Above pH 7, the rate of reaction of THP appears to be controlled by diffusion of the reagent into the fibers [75] and, like the reaction of mercaptans with hair, increases rapidly with increasing pH in the vicinity of pH 9 to 12. Presumably, this increase in reaction rate results from increased swelling of the keratin substrate with increasing pH.

The equilibrium constant for the reaction of THP with cystyl residues in hair must be relatively large, since essentially complete reduction of human hair occurs with only a ten-fold excess of THP, at neutral pH [77].

4.6.6 *Miscellaneous Reducing Agents*

Borohydride (MBH_4) has also been used as a reducing agent for keratin fibers [78, 79], as well as dithionite ($M_2S_2O_4$)—sometimes called hydrosulfite [45]. Sulfoxylate (M_2SO_2) [80] or, more correctly, its ester salts—e.g., sodium formaldehyde sulfoxylate ($HO\text{-}CH_2\text{-}SO_2Na$) a weak reducing agent is used as a reductive bleach to lighten natural wool and is not an effective permanent waving agent.

4.7 Reactions of the Mercaptan Group

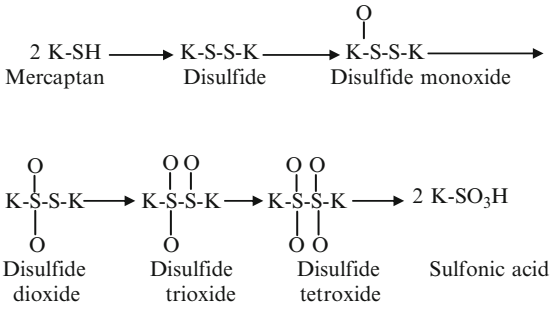
The previous section described various reagents that have been used for the reduction of the disulfide bond in keratin fibers. Most of these reactions produce cysteinyl residues, or mercaptan groups in the fibers.

The mercaptan group is one of the most reactive functional groups in all organic chemistry, and it readily undergoes oxidation, nucleophilic displacement, nucleophilic addition, and free-radical addition and displacement reactions. This section discusses some of the chemical literature pertaining to these types of reaction in reduced keratin fibers, and illustrates the potential reactivity of the mercaptan group in human hair.

4.7.1 *Oxidation of Reduced Keratin Fibers*

The oxidation of the mercaptan group can occur by two distinct pathways—the S-S fission route (pathway in the presence of most chemical oxidants), and the C-S fission route, the pathway for radiation-induced cleavage of the disulfide bond. Only the S-S fission route will be discussed in this section, because it is the most relevant pathway in relation to permanent waves and reducing agents. For a more complete discussion of both of these mechanistic schemes, see Chap. 5.

The oxidation of the mercaptan group can occur in several stages:



Among this group of compounds, mercaptan, disulfide, and sulfonic acid have been isolated from the oxidation of reduced hair [53], the principle products being either disulfide or sulfonic acid depending on the strength of the oxidizing agent used. Since the primary intent in the oxidation of reduced hair in permanent-waving is to stop at the disulfide stage, milder oxidizing conditions are used than for bleaching hair. Some of the reagents that have been used for oxidation of reduced hair are bromates [81, 82, 83], iodate [85], perborate [84], acidic hydrogen peroxide [53], monopersulfate [85], and even air oxidation or metal-catalyzed air oxidation [79].

4.7.2 Nucleophilic Displacement

The mercaptan group is an extremely powerful nucleophile and it readily undergoes nucleophilic displacement reactions [86, 87]. This property is the basis of several quantitative tests for cysteine and/or cystine, including the Sullivan test, which involves nucleophilic displacement by mercaptide ion on iodoacetate [88].

Iodoacetic acid

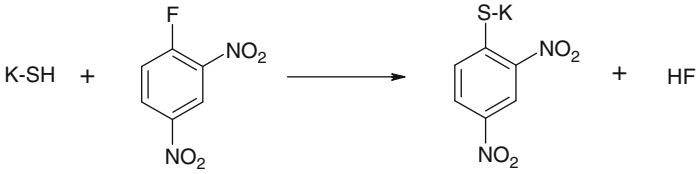
Methyl iodide has been used as a mercaptan blocking group in studies on keratin fibers [89]. Other monofunctional alkyl halides, including benzyl chloride, heptyl bromide, and dodecyl bromide, have also been reacted with reduced keratin fibers [8]. Hall and Wolfram [90] have used this reaction (alkyl iodides with reduced hair) as a means to introduce alkyl groups or non-polar residues into hair. These researchers found that methyl iodide was highly efficient in reacting with the mercaptan groups of reduced hair. Longer chain-length alkyl iodides, however, were not nearly as efficient for introducing alkyl groups into reduced hair.

alkyl halide

The Bunte salt grouping has also been reacted with mercaptan in reduced keratin fibers [91] to form a mixed disulfide.

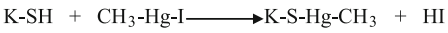
Bunte salt

Reaction of activated aryl halides, such as 2,4-dinitrofluorobenzene, with cysteine in unreduced and in reduced hair has been described by Zahn [53] as a quantitative assay for mercaptan and/or disulfide in keratin fibers.



Dinitrofluorobenzene

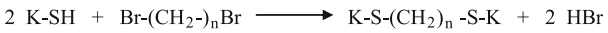
Halo mercury compounds such as methyl mercuric iodide also react readily with mercaptan in keratin fibers [92] and serve as the basis of Leach's method for cystine analysis.



Methyl mercuric Iodide

In fact, mercaptan in hair is capable of reacting with disulfide monoxide by nucleophilic displacement [93] or with most compounds that contain a group labile to nucleophilic displacement, if such labile groups are either formed in the hair or capable of diffusing into the hair.

Molecules containing two leaving groups similar to the previously described monofunctional compounds are capable of reacting with reduced keratin fibers and forming a new type of cross-link. Dihaloalkanes have been reacted with reduced wool fiber to provide a thioether cross-link [8]. This reaction is capable of promoting stability to moths in wool [94], thus confirming that the primary site that moths attack in wool fiber is the disulfide bond.



Dihaloalkane

Di-Bunte salts have also been used to re-cross-link reduced keratin fibers through a bis-disulfide type of linkage [91, 93].

Di-Bunte salt reaction

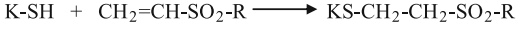
Other rather exotic bi-functional reagents have been reacted with both reduced and unaltered wool fiber and are described in Section C of the Proceedings of the International Wool Textile Research Conference (1955).

4.7.3 Treatment of Reduced Hair with Dithioglycolate Ester Derivatives of Polyoxyethylene

A novel treatment in permanent waving involves reacting reduced hair with polyoxyethylene esters of thioglycolic acid (mol. wt. 550–750) described by Salce et al. [95]. These esters are reported to bind to the fibers by displacement of reduced disulfide in hair on the ester linkage of the additive resulting in the formation of mixed disulfides, producing more hydrophobic hair fibers and improvement in the curl relaxation due to the increased hydrophobicity.

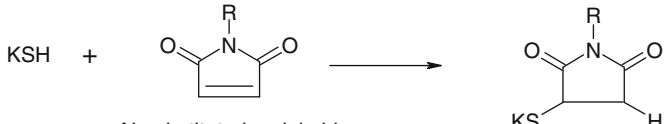
4.7.4 Nucleophilic Addition Reactions

Mercaptan groups in keratin fibers also undergo nucleophilic addition reactions with active olefins (olefins containing a strong electron-withdrawing group attached to the double bond). Schoberl [93] has shown that reduced wool fiber reacts with vinyl sulfones.



Vinyl sulfone

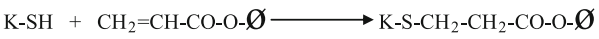
Maleimides are another example of activated olefins that react in this manner—e.g., N-ethyl maleimide (NEMI) [93, 96] reacts quantitatively with the mercaptan groups in reduced keratin fibers by a nucleophilic addition type reaction. Hall and Wolfram [90] have used this reaction to introduce N-substituted maleimide groups (N-ethyl, N-hexyl, and N-heptyl maleimides) into human hair to study the properties of hair modified by the introduction of non-polar residues. They report enhanced settability and high set retention, at all humidities, for hair modified in this manner with greater than 50% disulfide cleavage. However, hair having less than 50% disulfide scission does not show improved set characteristics.



N-substituted maleimide

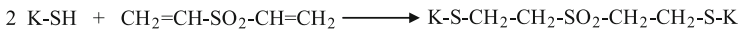
Acrylonitrile and phenyl acrylate have also been shown to react readily with the mercaptan groups of reduced hair [96].

Acrylonitrile



Phenylacrylate

Bi-functional reagents containing two active vinyl groups are capable of reacting with reduced keratin fibers and forming cross-links. Divinyl sulfone has been used for this purpose [93].



Divinyl sulfone reaction with keratin fibers

4.7.5 Free-Radical Addition and Polymerization Reactions

One form of polymerization that has been used in the chemistry of wool fiber involves reduction of the fibers followed by the addition of a vinyl monomer and an oxidizing agent [97, 98]. These reactions have been carried out in an inert atmosphere and provide rather large polymer add-ons. Related procedures have also been described for polymerizing into human hair in an air atmosphere and are described in detail in Chap. 8 [99–101].

In this type of reaction, the mercaptan group of the reduced keratin may serve as the reducing agent in a redox system for generating free radicals. The mercaptan group may also serve as a site for grafting, and it can serve as a chain transfer agent, limiting the degree of polymerization. Another advantage to this system is the increased swelling of the fibers accompanying reduction. This effect facilitates diffusion of all reagents necessary to polymerization into the fibers. (For additional details, see Chap. 8.)

Polymerization into wool fiber has also been accomplished using radiation grafting techniques [102, 103], although no such procedures could be found using human hair as substrate.

4.8 Water Setting Human Hair

If human hair is wet with water and held in a given configuration while drying, it will tend to remain in that configuration. This is the basis of what is called a water-set in human hair. It is well known; however, that exposure of water set hair to high humidity produces a loss of set. Recently, Diaz and co-workers [104] have demonstrated that exposure of water-set hair tresses to a lower humidity can also

Table 4.2 Low humidity effects on curl retention (all fibers set and dried at 60% RH)

Time exposed	Percent curl retention	
	60% RH	10% RH
2 h	73.5%	61.3%
24 h	59.6%	58.3%

produce a loss of set. In addition, Robbins and Reich [105] have demonstrated this same phenomenon with single hair fibers.

Table 4.2 summarizes one of the single-fiber experiments. Single hairs were water-set in a curled configuration on glass rods and dried at 60% RH. After removing the fibers from the rods, one group of hairs was exposed to a 60% RH atmosphere and another to 10% RH. Curl length was measured over time with a cathetometer.

The data in Table 4.2 were then analyzed by repeated measures ANOVA. Highly significant time effects, significant humidity effects, and significant interactions were found. Therefore, one may conclude that changing the environment of single hairs that have been water-set at a higher humidity (60% RH) to a lower humidity causes more rapid curl loss in short time intervals (2 h) than maintaining the hair at the higher humidity. This more rapid curl loss occurs in spite of the fact that hair equilibrated at a lower humidity will contain less water [106] and exhibit greater bending [107] and torsional stiffness [108] than hair equilibrated at a higher humidity.

The fibers when taken from 60% to 10% RH lose water until they re-equilibrate with the new environment (approximately 16% moisture at 60% RH to 5% moisture at 10% RH [106]). During this transition stage, as water migrates out of the fibers, hydrogen bonds are broken and reformed, and more rapid curl loss (set loss) occurs.

At the longer time interval (24 h), the hair fibers that were maintained at the higher humidity are equal (in curl retention) once again to the fibers transferred to the lower humidity. Apparently, after equilibration of moisture at the lower humidity, the rate of curl loss becomes less than for hair maintained at the higher humidity allowing the curl loss to equalize. Presumably at even longer times, the curl loss for the hair at the lower humidity would be less than for the hair at the higher humidity.

Diaz's experiments were with hair tresses and in a sense were more pragmatic than the single-fiber experiments; however, they include inter-fiber complications excluded from the single-fiber test. Fiber friction increases with RH for keratin fibers [108], and effects from frictional contributions tend to enhance the set stability of the hair at the higher humidity. Nevertheless, Diaz's results indicate the same general picture as with single hairs. Therefore, these two types of experiments complement each other with regard to providing a better understanding of the mechanism of water-setting human hair.

The following important insights are reflected in these results: Exposure of water-set hair to changes in humidity results in moisture either entering or leaving the fibers. The flow of or transfer of strongly bound water either into or out of hair produces cleavage of critical hydrogen bonds resulting in a decrease in water-set

stability. The behavior of hair equilibrated at different humidities may not reflect its behavior during the transition to different humidities, and changes in humidity are probably more likely to be encountered in the real world than constant humidity.

Water-setting hair provides a temporary reversible set to hair, because hydrogen bonds are involved. Therefore, a water set can be removed from hair by the transfer of moisture either into or out of hair. Permanent waves, in contrast, are more resistant to moisture transfer into and out of hair, because covalent bonding (the disulfide bond) and other molecular changes are involved and covalent bonds are relatively inert to moisture changes in hair.

4.9 Set and Supercontraction

Set has been defined by Brown et al. [109] as a treatment that enables a keratin fiber to maintain a length greater than its original length. As a contrast, supercontraction is the condition in which a keratin fiber is fixed at a length less than its original length [109]. Set is usually determined by a procedure similar to the one described by Speakman [58]. Fibers are stretched to 40%, treated, then rinsed and tested for their ability to retain the extended length when placed in water or buffer at elevated temperatures. The criterion for "permanent" set is the resistance to lengthwise shrinkage in boiling water. Supercontraction can also be followed by observing lengthwise changes in full-length fibers or by microscopic observation of fiber snippets [110].

The setting process is generally considered a three-stage process. Stage 1 is the stretching stage. Stage 2 is the period of structural rearrangement, consisting of the time period that the fibers are held in the stretched state. Stage 3 is the recovery period, the time after the external strain is removed.

Widely varying reaction conditions and gross alterations to the fibers have been made during the course of the study of the mechanism(s) of setting, although it appears that most of the literature on setting is concerned with establishing a single common mechanism for all treatments. Jenkins and Wolfram [111] suggested and provided evidence indicating that more than one mechanism may exist for setting keratin and highly altered keratin fibers. The discussion in this section is primarily concerned with the conditions of wool setting that are related to the permanent-waving process. Therefore, a single mechanism is considered.

When keratin fibers are stretched in an aqueous medium in the presence of a reducing agent, several bonds are broken owing to internal stresses resulting from the imposed strain. Hydrogen bonds are broken, their resistance to the imposed strain decrease with increasing temperature [101]. The importance of hydrogen bonds to stage 3 (recovery) and to structural rearrangement (stage 2) has been demonstrated. Farnworth [112] showed that urea plus, a reducing agent, is capable of producing permanent set in keratin fibers under conditions in which neither reagent alone will produce permanent set. Therefore, the breaking of additional

hydrogen bonds by urea permits structural rearrangements to occur in the presence of a reducing agent that reduction alone cannot achieve.

Weigmann et al. [113] and Milligan et al. [114] have clearly demonstrated the importance of the disulfide and mercaptan groups to all three stages of the setting process. Elimination of mercaptan before stretching prevents permanent set. On the other hand, permanent set is enhanced by elimination of mercaptan before releasing stretched fibers. Interestingly, mercaptan elimination in the latter circumstance may be accomplished either by re-oxidation to the disulfide or higher oxidation products, or even by blocking mercaptan with active reagents such as iodoacetate [114]. In fact, Menkart et al. [115] have suggested that a larger amount of set results from blocking mercaptan than from re-oxidation to disulfide. This suggestion is very reasonable because blocking mercaptan permanently blocks disulfide mercaptan interchange but re-oxidation to disulfide does not permanently prevent the interchange.

These experiments collectively demonstrate that structural reorganization during the setting of keratin fibers in aqueous reducing agents is facilitated not only through disulfide bond breakdown but also, to a large extent, through disulfide-mercaptan interchange reactions.

Since keratin fibers undergo crystallographic changes on stretching, X-ray diffraction can be used as a tool to study the setting mechanism. Setting of human hair by various means produces an alpha to beta transformation [84]. Therefore, setting hair is clearly different from water setting which involves small reversible deformations and only hydrogen bond breakage. Therefore, during setting some of the alpha helices of the filamentous regions of the cortical cells are stretched, and a beta configuration is formed. A number of forces including covalent bonds, hydrogen bonds, salt linkages, Van der Waals forces, and steric interferences oppose stretching and setting. The weak links in these "chains of forces" opposing strain probably exist primarily in the matrix of the cortex, the disulfide bonds in the intermediate filaments and in the A layer and exocuticle of the cuticle.

Certainly in aqueous reducing solutions, the weakest links in these "chains of forces" are the disulfide bonds and those associated hydrogen bonds that are broken and interchanged. These are the actions that permit the structural rearrangements in the microfibrils and other structural rearrangements that are critical to setting. However, as pointed out by Wortmann and Souren [1] a main effect of reduction or the breakage of disulfide bonds in setting must be on the crystalline filaments, that is on the interactions between the crystalline structures and the reorganization that occurs involving those structures rather than on the disulfide bonds themselves.

In addition to cortical changes, extensive changes occur in the cuticle during permanent waving. Wickett and Barman [11] have demonstrated that a satisfactory permanent wave can be achieved by greater cuticle/cortex reduction than with existing thioglycolate waves. The A layer and exocuticle contain high concentrations of cystine residues [116] and are therefore highly reactive to reducing agents. The endocuticle, on the other hand, contains relatively little cystine [116]. Therefore the primary reaction of the reducing agent in the cuticle will be with the stiff resistant

A layer and exocuticle regions. These stiff cuticle layers will be softened allowing for structural rearrangement. Upon re-oxidation, the macromolecules of the A layer and exocuticle layers will be re-hardened to a new configuration. Thus a combination of cortical and cuticle changes occurs in permanent-waving to provide a new "permanent" shape to the keratin fiber consistent with the observations of Wortmann and Kure [2, 3].

One might also anticipate greater cuticle contribution to a permanent wave in fine hair as compared to coarse hair, because of the greater ratio of cuticle to cortex in fine hair; see Wolfram and Lindemann [117]. This is because thin and coarse hair contains the same number of cuticle layers, with essentially the same thickness. Therefore, fine hair contains a greater proportion of cuticle to cortex than coarse hair. Assuming a 4-micron-thick cuticle, for coarse, 100-micron-diameter hair fibers the cuticle would comprise only 15% of the fiber cross section. However, for thin, 40-micron hair fibers, the cuticle would comprise 36% of the total fiber cross-section.

Fine hair is known to be resistant to waving. This effect is likely due to its high cuticle content. Wortmann and Kure [2] have demonstrated that the cuticle decreases the rate of reduction of hair fibers and it most likely plays a role in the permanent set of human hair due to its stiffness. The cuticle may play a lesser role than the cortex in permanent waving, nevertheless, it is difficult to conceive of the cuticle not playing an important role in waving reactions that involve reduction, shaping, and re-hardening of the high-sulfur A layers and exocuticle layers.

Hair swelling agents, such as concentrated solutions of alkali metal halides [118] or aqueous solutions of reducing agents [119], are capable of promoting supercontraction as well as setting; see the section on hair straightening in this Chapter. The types of reagents that promote supercontraction suggest that hydrogen bond breakage is important to supercontraction. Burley [120] has shown that disulfide-mercaptan interchange can also be involved in supercontraction. In addition, keratin fibers, while undergoing supercontraction, suffer a loss in birefringence, and the alpha-X-ray diagram disappears [121, 122]. This suggests molecular reorientation in the filamentous regions of the cortex. The alpha keratin is thus rearranged to a less organized structure. Therefore, supercontraction, with the exception of the driving force, and the final molecular orientation is very much related mechanistically to the process of setting.

In the first edition of this book, I proposed that one might consider the curling (waving) of a human hair fiber as a combination of setting and supercontraction. A bent hair fiber that is treated with an aqueous solution of a reducing agent is undergoing concomitant extension (setting) and compression (which should be more analogous to supercontraction than to setting). If one perceives the waving or straightening of human hair in this manner, one may then apply the testing procedures and mechanisms for these two phenomena to arrive at a picture of the waving process. In the future, perms and straighteners that are more resistant to washout are possible by developing compositions that provide for more extensive molecular conformational changes (loss of alpha keratin structure) as described by Wong et al. [123] for alkaline hair straighteners.

Wortmann and Kure [1] have been able to provide a model that explains the set behavior obtained in the permanent waving of human hair in terms of the bending stiffness of single hairs during the reduction and the oxidation reactions. Wortmann and Kure propose a distribution of Young's moduli from the hair surface to the center of the fiber and a diffusion controlled breakdown during reduction. This model is simple, yet elegant, and it is highly satisfactory in spite of the fact that it does not consider the two-phase composite nature of the cortex of human hair. Feughelman [4] extended this model, by proposing a model for setting a bent fiber and taking into account the two-phase composite nature of the cortex of keratin fibers.

Even though the criterion for permanent set in the wool industry is markedly different from that in the hair-waving industry (boiling water vs. neutral pH shampoos near room temperature), much can be gained in the understanding of hair waving and straightening by using the test procedures employed for wool and by drawing analogies to the mechanisms of setting and supercontraction.

4.10 Swelling: During and After Treatment

The microscopic method (change in volume) [124] and the centrifugation method (change in weight) have been used for studying the swelling of human hair by aqueous solutions of mercaptans. Both the rate and the extent of the swelling of human hair by mercaptan solutions are pH-dependent and increase dramatically with increasing pH above neutrality [29, 125]. At high pH, using a high solution-to-hair ratio, swelling in excess of 300% is possible with thioglycolic acid even at relatively short reaction times [125]. The swelling of human hair in aqueous mercaptan solutions is a direct reflection of the chemical reactions occurring inside the fibers and can therefore be described in terms of the reactivity considerations outlined in the section on the kinetics of this reaction.

Shansky [126] studied the swelling action of hair fibers during reduction, rinsing, and chemical neutralization—i.e., a simulated cold wave process. During the reaction with mercaptan, the swelling action is extensive. Upon rinsing, swelling continues, but at a reduced rate. This decreased swelling rate is attributed to osmotic forces arising from the rapid decrease in salt concentration outside the hair compared to inside the fiber. During neutralization, de-swelling occurs.

Hair fibers reduced and re-oxidized approach the original fiber diameter. Eckstrom [124] suggested that the milder the conditions of reduction, the closer the fiber will return to its original dry-state diameter on neutralization.

Fiber diameter determined in the wet or swollen state is sensitive to changes produced by damaging treatments like permanent waves or bleaches. The swelling action of permanent-waved hair [29] and bleached fibers [31] is greater than in unaltered hair and has been used to estimate the extent of alteration produced by reduction and re-oxidation [30]. For additional discussion on hair swelling, see Chaps. 1 and 9.

4.11 Permanent Waving of Human Hair

Charles Nessler is a key figure in the invention of the permanent wave in London in 1905 [127]. The first permanent waves were concentrated solutions of alkali (5–15%) or alkaline sulfites [127, 128] that reacted with hair at elevated temperatures. In these treatments, high temperatures were achieved by using curling irons, chemical heating pads, or electric heaters [129].

Current permanent waves are vastly superior to the early hot waves and do not require elevated temperature; thus the designation "cold waves." Cold waves became successful during World War II and have not changed substantially for nearly 70 years. These products are based on mercaptans or sulfites, the most common of these being thioglycolic acid, which is generally employed at a concentration of approximately 0.6 N and a pH of 9 to 9.5.

Sulfite waves employ a pH near 6 and a hydrogen peroxide neutralizer. This type of product generally claims to provide a wave that does not "frizzle" the hair, i.e., is gentle to your hair, and can be used on any type of hair (damaged or undamaged) [130]. This image is consistent with the fact that sulfite is a weaker reducing agent than thioglycolate (see the discussion on the reduction of hair by sulfite earlier in this Chapter).

Thioglycolate and sulfite waves are the primary reducing agents used in home permanent waves today. Although as indicated, glycerylmonothioglycolate (GMT) and cysteamine hydrochloride are being used in the professional field in commercial acid waves or waves that are formulated closer to neutral pH. GMT requires a covering cap and the heat of a dryer to accomplish sufficient reduction to provide a satisfactory permanent wave [26].

4.11.1 Cold Wave Formulations and Making Cold Wave Products

A typical thiol permanent wave consists of two compositions. The first, a reducing solution often called a waving lotion, is a composition similar to that in Table 4.3. To make this permanent wave formulation, first melt the emulsifier/wetting agents (steareth-20) and add them to oxygen free water, under an inert atmosphere, at

Table 4.3 A thiol permanent wave waving lotion

Ingredient	Percent
Thioglycolic acid	6.0
Steareth-20	2.5
Fragrance	0.5
Ethylene diamine tetraacetic acid	0.2
Colors	As required
Water	q.s.[a]
Ammonium hydroxide	To pH 9.3

[a]q.s., add water to 100%

Table 4.4 Neutralizer for a permanent wave product[a]

Ingredient	Percent
Hydrogen peroxide (30%)	7.0
Polysorbate-40	2.5
Phenacetin	0.5
Water	q.s.[b]
Phosphoric acid (85%)	To pH 4

[a]For making the neutralizer (Table 4.4), heat the water to 75° and melt the polysorbate-40 and slowly add it to the water with stirring. Cool to room temperature and then add the peroxide, the phosphoric acid and the preservative
[b]q.s., add water to 100%

Table 4.5 Waving lotion for softwave formulation

Ingredient	Percent
Ammonium bisulfite	4
Ammonium sulfite	3
Laureth-23	2.5
Fragrance	~0.5
Water	q.s.[a]
Ammonium hydroxide	To pH 8

[a]q.s., add water to 100%

about 50° while stirring. Cool to room temperature. Add about 3% concentrated ammonium hydroxide, then add thioglycolic acid with stirring. Add other ingredients and adjust the pH with ammonium hydroxide or the preferred form of alkalinity.

Consider the following precautions for making thiol perms. One should use a lined vessel [glass, plastic (polyethylene or teflon or other inert plastic) or stainless steel]. One should avoid contact with all metals, because thiols react with many metals to form colored salts. Note, salts of thioglycolic acid may be handled in stainless steel, but thioglycolic acid may not. Also minimize heat whenever thioglycolic acid is present. Exposure to air and oxygen should be avoided, for example use oxygen free water and package with a minimum of headspace, because thiols are sensitive to air oxidation (Table 4.4).

A milder waving lotion sometimes called a softwave (Table 4.5) can be made in the following manner. Add the laureth-23 to water at 70° with stirring. Cool to room temperature and dissolve the bisulfite and the sulfite. Then add the fragrance and adjust the pH to 8 with ammonium hydroxide. Oxygen free water should be used and the mixing in an inert atmosphere. For the softwave product, the neutralizer described above in Table 4.4 for the ammonium thioglycolate wave can also be used.

4.11.2 Acid Waves

Acid waves are generally based on glycerolmonothioglycolate (GMT) although some bisulfite systems are also sold as acid waves. For a GMT wave, the waving

Table 4.6 Waving lotion for an acid wave based on GMT[a]

Ingredient	Percent
Part I	
Glycerol thioglycolate (GMT) (75%)	77.3
Glycerine (oxygen free dry glycerine)	22.7
Part II	
Urea	4.1
Neodol 91–8	1.0
Dodecyl benzene sulfonate	0.5
Triethanolamine	0.8
Potassium sorbate	0.35
Ammonium carbonate	0.2
Disodium EDTA	0.2
Water (oxygen free)	q.s.[b]

[a]The neutralizer described in Table 4.4 can also be used with this product
[b]q.s., add water to 100%

lotion itself consists of two parts because GMT is not stable for long periods of time in water.

To make the acid wave, for Part I of the waving lotion described in Table 4.6, add glycerol thioglycolate to glycerine (oxygen free) in an inert atmosphere taking the same precautions as described for the thiol wave. For Part II of the waving lotion, dissolve the sulfonate and the neodol in water; then add the remaining ingredients in the order listed in the formula. Immediately before application to the hair, mix parts I and part II of the waving lotions.

Other cold-wave formulations and related products are described by Gershon et al. [130], and by Flick [131, 132]. Product ingredient labels provide the most up-to-date qualitative information on these types of products.

4.11.3 Properties of Cold-Waved Hair

The chemical changes produced in hair by permanent waving, as indicated by amino acid analysis, are quantitatively small and do not reflect the vast structural changes that have taken place in the fibers during a permanent wave. Small decreases in cystine [53, 54, 133] and corresponding increases in cysteic acid [53, 54, 133] and in cysteine [53, 54] have been reported. Small quantities of mixed disulfide [133], sorbed thioglycolic [53], and dithiodiglycolic acids [133] have also been detected in hair that has undergone cold-waving treatments. Zahn et al. [134] also demonstrated small quantities of intermediate oxidation products of cystine in permanent-waved hair. For additional details of the chemical changes occurring in hair that has undergone permanent waving, see Chap. 2.

The wet tensile properties of hair are decreased by permanent waving. However, the dry tensile properties remain virtually unchanged; see Chap. 9 for

additional details. The torsional behavior of hair that has been permanent-waved is also changed. Bogaty [135] demonstrated that waved hair is more rigid in the dry state yet less rigid in the wet state than unwaved hair. Schwartz and Knowles [136] determined that the frictional resistance of human hair is increased by permanent waving providing evidence of changes (damage) in the cuticle of hair. Increased fiber friction results in more difficult combing of hair that has undergone permanent-wave treatment. For additional details on the changes in these properties, see Chap. 9.

The swelling capacity of permanent-waved hair increases in proportion to the damage rendered by the waving process [124]. Increased swelling is evidence of cuticle and cortical damage to hair. Greater swelling produces a substantial increase in the chemical reactivity of hair toward those reactions in which diffusion is rate-limiting. And since most of the whole-fiber chemical reactions that human hair undergoes are diffusion-controlled, permanent waving can markedly alter the chemical character of human scalp hair.

4.11.4 The Nature of the Cold-Wave Process

4.11.4.1 The Reduction Step

A very important factor in cold-waving hair on heads is the solution-to-hair ratio, which is limited by the capillary spaces between the fibers, and the amount of solution absorbed into the hair excluding solution runoff. Assuming a solution to hair ratio of 2:1 for a two-fold addition of reducing solution to hair, a 0.6 M mercaptan solution, and a favorable equilibrium constant (for thioglycolate at alkaline pH), there is insufficient mercaptan for total reduction of the disulfide bonds in hair. Randebrook and Eckert [137] and Reed et al. [138] suggested that only about 20% of the cystine in hair is reduced during an average thioglycolate permanent-wave treatment. Less reduction occurs for an average sulfite wave.

During the reduction step, a highly reduced zone proceeds into the cuticle and eventually into the outer regions of the cortex. This leaves an inner zone of unreduced hair. The relative quantities of reduced vs. unreduced fiber depend on the reducing agent (thioglycolate vs. sulfite), its concentration, the solution-to-hair ratio, pH of the reaction medium, time of reaction, fiber diameter, and the condition of the hair; variables which, for the most part, have already been considered in this Chapter. For another useful discussion of the waving process, see the article by Gershon et al. [130].

The relatively high cleavage of cystine residues and the resultant high concentration of cysteinyl residues produced from the reaction of thioglycolic acid or sulfite with hair and the physical stress from curling the fiber produce molecular reorientation that is facilitated by disulfide-mercaptan interchange. Reduction occurs in the high-sulfur regions of the fibers, i.e., the A layer and exocuticle of the cuticle and the matrix and intermediate filaments of the cortex, permitting

molecular reorientation and structural changes to occur in both the cuticle and cortex, as described in the section on setting and supercontraction. Molecular changes including reorientation in the intermediate filaments are believed to be very important to the cold wave process as suggested by Wortmann and Souren [3]. However, changes in the high disulfide regions of the cuticle are also involved as demonstrated by the relationship of fiber stiffness and the gradient of stiffness changes involved in the permanent wave process as shown by Wortmann and Kure [1, 2].

4.11.4.2 Rinsing

Cessation of the reduction reaction and removal of most of the reducing agent to minimize hair damage is the primary function of rinsing. The continued increase in swelling during the rinse by osmotic forces has already been described.

4.11.4.3 Creep Period

After rinsing, the hair is often wrapped in a towel and maintained in the desired configuration for a given period of time (up to 30 min). This step has been called the "creep period" and was introduced into the waving process in the early 1950s [139]. Continued molecular reorientation through disulfide-mercaptan interchange and secondary bond formation (other than covalent bond formation) occurs during this step. Since secondary bonds contribute to wave stability [140], this step is important to the total permanent-wave process.

4.11.4.4 Neutralization

Neutralization or re-oxidation is accomplished primarily through chemical means such as by mild oxidation for thioglycolate waves or mild oxidation or mild alkali for sulfite waves. Neutralization rapidly decreases the mercaptan content in the fibers, decreasing the probability of disulfide-mercaptan interchange, and thereby stabilizes the permanent wave.

4.12 Hair Straightening and Hair Straightener Products

4.12.1 Hair Straightener Compositions

During the past century, several different types of products have been used to straighten curly to kinky hair. In this discussion, we will consider five different types of products/processes used for this purpose.

Gums, resins or waxes are used to temporarily straighten the hair by plastering it down. These are generally very simple mixtures such as petrolatum and waxes or paraffins or even more complex waxes, gums or resinous ingredients with fragrances. Obviously, these products do not alter the hair chemically, and thus, are not permanent straighteners.

Hot combs and straightening irons have been widely used for straightening hair. In fact, some people actually iron their hair straight with a clothes iron. Straightening irons sometimes called crimping irons or curling irons generally are electrically heated crimping devices that open and are then clamped on the hair to remove or add curl. Oftentimes, petrolatum based oils called pressing oils are used in conjunction with the iron or the hot comb to lubricate the hair so the device can slide more easily through the hair and thus facilitate this process. These oils usually contain waxes and hair conditioners in a petrolatum base that is perfumed. This type of process produces only temporary straightening, functioning partly through cohesive and adhesive forces in a highly viscous system to help keep the fibers parallel.

Alkaline based straighteners, sometimes called chemical relaxers, are used primarily by men or by women with short hair and are the main permanent straightening products used today. Alkaline straighteners usually contain 1–10% sodium hydroxide, lithium hydroxide, calcium hydroxide or a combination of these alkaline ingredients or their salts. Alkaline straighteners are often sold as cremes containing conditioning ingredients such as stearic acid, cetyl and/or stearyl alcohol, mineral oil, etc. that thicken the product, see Table 4.7.

These alkaline hair relaxers are highly viscous creams. The high viscosity functions to help control run-off, because care must be taken to avoid contact with the eyes and minimize contact with the scalp to prevent alkaline burns. The hair should be washed prior to application. Product use instructions frequently recommend placing petrolatum along the hair-line and on the ears before application of the straightener. The product is then combed through the hair starting near the root ends, while combing away from the scalp. After processing, the hair is rinsed carefully under a running tap.

Table 4.7 An alkaline hair straightener[a]

Ingredient	Percent
Stearic acid	17
Oleic acid	3
Stearyl alcohol	2
Glycerine	5
Sodium hydroxide	9.5
Fragrance	0.5
Water	q.s.[b]

[a]Dissolve the alkali and glycerine in the water and then heat to 90°. Melt the stearyl alcohol and add it to the heated alkaline solution while stirring. Heat the acids to 95 and add to the aqueous emulsion while stirring. Cool and add the fragrance

[b]q.s., add water to 100%

4.12.2 Reactions of Hair Straighteners

The section of this Chapter entitled, *Side reactions during the reduction of keratin fibers with mercaptans*, summarizes the chemistry of the reactions of alkaline reagents with hair proteins. As indicated, alkalies react with cystine groups producing lanthionyl residues, a stable thioether crosslink. They also react with peptide bonds, hydrolytically cleaving this linkage, producing acid and amine groups. The reaction of alkaline species with amide groups of proteins produces acidic residues of aspartic and glutamic acids. Chemical hair straighteners and relaxers are among the top consumer complaint products including complaints dealing with hair breakage, hair damage and scalp burns. While many of these complaints are due to product misuse by either the consumer or a hair stylist, the incidence of complaints is still very high relative to other products.

Wong et al. [123] determined that alkaline hair straighteners provide the most permanent hair straightening. These authors examined ten different reagents for hair swelling, supercontraction and permanent hair straightening. They found that "permanent" straightening can be achieved only when the hair fiber has supercontracted more than 5%, see the data of Table 4.8. Furthermore, these scientists demonstrated that supercontracting agents like lithium chloride, which cause supercontraction with virtually no cystine reduction, can also produce permanent hair straightening. Therefore, they concluded that the molecular conformational changes that accompany supercontraction, e.g., part of which is the rearrangement of alpha-keratin to a less organized structure (see the Sect. 4.9) are more important to permanent hair straightening than the reduction reaction. Furthermore, this result also suggests that these molecular conformational changes are more important to this process than lanthionine formation.

The pH of alkaline straighteners varies from about 12 to above 13 and damage to the hair from these products is largely related to pH. Guanidine carbonate and calcium hydroxide are often used in combination in some products. A lithium hydroxide product with a pH as low as 12.8 can be made that is quite effective.

Table 4.8 Permanent straightening by several reagents and supercontraction

Composition	Straightening	Swelling	% Supercontraction
NaOH (1 N) pH 14	Permanent	>40%	5.7
NaOH (0.1 N) pH 13	Temporary	40%	0
THP (1 M) pH 8.5	Permanent	>50%	6
TGA (1.2 M) pH 9.6	Temporary	80%	2
LiCl (40%)	Permanent	60%	11.5
Boiling water	Permanent	>15%	6
DTT (0.8 M) pH 3.5	Temporary	>50%	0
Resorcinol (40%)	Permanent	>50%	10
Hot Press[a]	Temporary	–	0
Reduction/Hot Press[a]	Permanent	–	5–10

[a]Most of the above data is from Wong et al. [123] except for these two facts from the paper by Ogawa et al. [141]

Of course other additives are used to control the viscosity to make a safer and a more aesthetic product.

Wong et al. [123] demonstrated that for hair straightening, unlike permanent waving, the application of an external force is not necessary because the transitions that occur while the fiber is supercontracting provide sufficient stress to straighten the fiber. Furthermore, reducing solutions such as thioglycolic acid (TGA 1.2 M at pH 9.6) or dithiothreitol (DTT 0.8 M at pH 3.5) even though they cause extreme swelling (greater than 50% increase in diametric swelling) do not provide permanent hair straightening because they do not provide supercontraction beyond 2% (with the accompanying molecular rearrangements), see Table 4.8. Sodium hydroxide (1 N) can straighten hair in about 20 min but it takes more than 1 h to straighten hair with either LiCl or cuprammonium hydroxides, suggesting one reason for the superiority of sodium hydroxide to these other treatments.

Ogawa et al. [141], only a few years ago, provided additional insights into the mechanism of permanent hair straightening. These scientists demonstrated both by X-ray diffraction and high pressure differential scanning calorimetry that supercontraction of around 12.5% is accompanied by and is likely caused by the transformation of alpha-helical proteins to amorphous proteins (as explained by Wong et al., see Table 4.9). This irreversible molecular transformation stabilizes the straightened hair fiber providing permanence to hair straightening.

Ogawa et al. [141] confirmed the long known facts that reductive methods or hot irons when used separately provide only temporary hair straightening in which the hair will revert to its original curvature, or close to it, either by washing or on exposure to high humidity. However, these scientists demonstrated that by combining reducing solutions such as TGA or TGA/DTDG (dithiodiglycolic acid (DTDG)) followed by a hot press application immediately after the reduction that permanent straightening can be achieved. This is the basis for the process called Japanese hair straightening or Thermal Reconditioning. These scientists further demonstrated that this type of permanent straightening is also accompanied by the transformation of alpha-helical (crystalline) proteins to amorphous proteins. Thus, Thermal Reconditioning involves supercontraction of hair fibers (see Table 4.9).

Similar to Wong et al. [123], Ogawa and associates found 5–8% supercontraction as optimal for permanent straightening. With their reductive-hot press straightening systems, Ogawa et al. found that approximately 90% of the initial cystine content was retained in the straightened hair with about 10% additional cystine as cysteic acid, suggesting no lanthionine formation during this process. Lanthionine is formed from beta-elimination of cystine residues. Since cystine is

Table 4.9 Supercontraction and crystallinity of hair from Ogawa et al. [141]

	Degree of crystallinity	Percent supercontraction
Untreated hair	29%	0
Treatment 1	16%	8.4
Treatment 2	12.2	9.9
Treatment 3	5.8	12.5

fully accounted for, lanthionine could not be formed during this process. Also, since the lysine content was essentially unchanged by this reaction, no lysino-alanine cross-links are formed during this process either.

As mentioned earlier, another type of hair straightener is based on a reducing agent without the use of hot irons. This type of straightener is related compositionally to permanent waves. These are thioglycolate and sulfite based hair straighteners. The chemistry for these products is essentially the same as for the permanent wave based thioglycolate and sulfite based products. However, compositionally these products do differ subtly from permanent waves. The reducing solution of a hair straightener is often called a relaxer solution rather than a waving lotion. In general, relaxer solutions of hair straighteners are more viscous compositions than permanent waving lotions and thus often contain thickening agents. These are usually creams that are thickened with polymers such as carbopol, e.g., carbopol 941, or glyceryl monostearate, stearic acid or long chain alcohols, see the formula in Table 4.10. The relaxer solution of thioglycolate straighteners is also slightly lower in pH usually 8.8–9.1 as compared to 9.2–9.6 for permanent waving lotions. For straightening with this type of composition it is necessary to comb the hair straight while the hair is in the reduced state.

An even lower pH product is based on sodium sulfite or even ammonium bisulfite. The pH of this latter product can be as low as 7.6. As one might expect, this type of product is not as effective at straightening very curly hair as the alkaline straighteners and it must be left on the hair for a longer period of time (as long as 50 min) to be effective.

The neutralizers of thiol reducing hair straighteners (Table 4.10) are similar to those of permanent wave products and are usually based on hydrogen peroxide or

Table 4.10 Thiol based hair relaxer solution for a hair straightener product[a]

Ingredient	Percent
Glyceryl monostearate	15.0
Stearic acid	3.0
Paraffin	1.0
Sodium lauryl sulfate	1.0
Thioglycolic acid	6.6
Ammonium hydroxide	20.0
Fragrance	1.0
Water	q.s.

[a]Solution 1: Stir the glyceryl monostearate, stearic acid, paraffin, and sodium lauryl sulfate with 35 parts water and heat to 95 , until the mixture is homogeneous and then quickly cool to 50°. Solution 2: Add the thioglycolic acid to the remaining water under an inert atmosphere and then add ammonium hydroxide while cooling making certain the temperature does not go above 50°. Slowly add the thioglycolate solution at 50° to solution 1. Make final pH adjustments with ammonium hydroxide to pH 9.0. Quickly cool to 40° and add the fragrance and then add water to 100%

sodium bromate. The sulfite based systems use either a similar oxidizing neutralizer or an alkaline system described earlier. The higher viscosity for hair straighteners is to facilitate holding the hair reasonably straight. However, to effectively straighten the hair with these products one must periodically comb and stretch the hair straight.

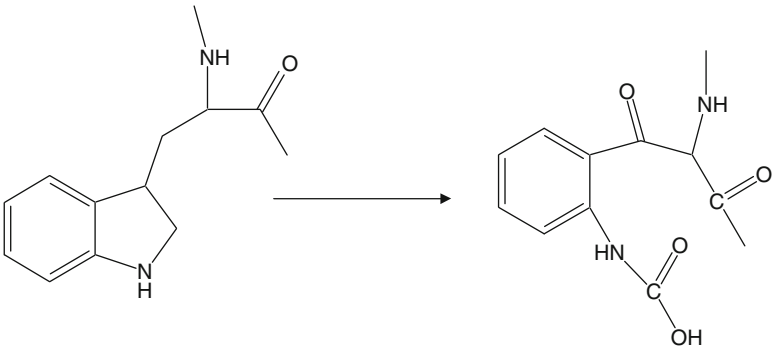
As indicated by the data of Table 4.8, the reductive type of hair straightener that does not employ hot irons does not provide supercontraction nor a loss of crystallinity. Therefore, it does not provide permanent hair straightening. In addition, this same redox chemistry when applied to a permanent wave provides more permanence for a wave than for hair straightening. The molecular rearrangements that produce permanent straightening and permanent waving (bending) involve some form of compressive forces on the fibers (supercontraction in bending) that either accompanies or facilitates the molecular rearrangements necessary for some permanent. Note that in reductive type straighteners extension or combing the hair is used and not bending as in a curl for waving and straightening is less permanent than waving.

4.12.3 Damage by Hair Straightening Products

The wax, resinous petrolatum type of hair straighteners do not alter the hair chemically and do not damage it. When used with lubricating oils, these products can help prevent damage to the hair. On the other hand, hot combs and straightening irons or curling irons are also temporary hair straightening or curling treatments, but these products can damage the hair [142]. Of course the reductive hair relaxer products also damage the hair and despite their advertising Japanese hair straightening also damages hair. However, the alkaline hair straightening products are the most damaging of all hair straightening products.

4.12.3.1 Damage by Heat Straightening

Thermal treatments have been shown to produce decomposition of tryptophan residues to kyneurenine type oxidation products, both thermally and via oxidation. In addition, thermally induced changes produce yellowing of white hair and bleached hair shows a slight darkening from thermally induced changes [142]. These color changes most likely arise from further oxidation of the above kyneurenine products. Furthermore, treatment of hair tresses either by a single or multiple treatments reveals a gradual increase in combing forces as a function of thermal exposure time.



A tryptophan residue in hair Opening of the tryptophan ring to a Kyneurenine product

Even though most of the thermal studies of hair have involved Caucasian hair or wool fiber [142–149] the chemical changes that occur on straight to wavy Caucasian hair or to curly to highly coiled African hair should be relatively similar. However, less degradation of tryptophan occurs with heavily pigmented hair vs. lightly pigmented hair of the same type [142]. This effect suggests a retardation of the thermal degradation of these chromophoric reaction products and a similarity to photochemical degradation of these same amino acid residues in hair. Furthermore, it suggests that thermal degradation of tryptophan likely involves free radical attack.

After thermal treatments, hair switches generally show a small decrease in combing forces [142]. However, after shampooing the combing forces are distinctly higher than for control hair. These effects were explained by thermal treatments that drive lipid material to the hair surface that is removed by shampooing, thus drying out the hair and unmasking surface damage to the fibers [142].

4.12.3.2 Damage by Reductive Hair Straighteners

Damage by reduction-oxidation type hair straighteners should produce damage similar to that of reduction-oxidation permanent wave products providing a decrease of about 5–20% in the wet tensile properties [150]. The chemistry of the reactions of permanent waves with hair involves reduction of disulfide bonds, followed by molecular shifting produced by stressing the hair on rollers followed by re-oxidation. The chemistry of reduction-oxidation hair straighteners is similar involving reduction of disulfide bonds and molecular shifting produced by stressing the hair by combing it straight followed by re-oxidation. One unanswered question is how much damage is done to the hair by combing it straight in the reduced state. The question involving a lack of permanence in straightening African American hair by a reduction-oxidation system was addressed in a previous part of this Chapter.

For the reduction step by this type of hair straightener, most of the commonly used reducing agents for hair have been used, the primary ones being TGA and sulfite. Albrecht and Wolfram [52] suggested that for low cleavage levels, sulfite is a more effective setting agent than thioglycolate, but at higher cleavage levels, thioglycolate is the most effective reducing g agent.

The pH of relaxer solutions of TGA hair straighteners is generally slightly lower (pH 8.8–9.1) than in permanent waving lotions (pH 9.2–9.6). Lower pH produces less disulfide cleavage and at low cleavage levels less hair damage results. So to minimize damage for this type of product sulfite is the preferred reducing agent. In addition, stressing the hair by combing it straight is a less controlled action than curling the hair on rollers. Therefore, considering only hair damage sulfite would be the preferred reducing agent.

The re-oxidation step with thiols usually involves mild oxidizing agents (sodium bromate or hydrogen peroxide) or when sulfite is the reducing agent, effective reformation of cystine can be achieved with alkaline solutions generally above pH 8, which reverses the sulfitolysis reaction below reforming cystine disulfide:

$$\text{K-S-S-K} + \text{M}_2\text{SO}_3 \rightleftharpoons \text{K-S-SO}_3\ \text{M} + \text{K-S}^-\ \text{M}^+$$

From the perspective of tensile damage, I would expect similar tensile damage from hair straightening and a permanent wave [150]. However, I would add the caution that more damage could be produced from "misuse" of the products and a lack of care during combing hair in the reduced state. I could not find any scientific literature that directly examines the tensile properties of African American hair treated with reduction-oxidation type hair straighteners. However, a reference by Kamath et al. [151] compared a reduction straightener without oxidation with an alkaline straightener and determined the fatiguing properties of the fibers showing greater damage to the African type hair from the alkaline straightener, see Table 4.11.

The hair used in this study was from a Black male age 31 and had never been treated with chemical or heat relaxers. After shampooing rinsing and drying, half of the fibers were treated with a commercial alkaline creme relaxer, stroking the product through the hair with the fingers for 20 min and then rinsing and shampooing. The other half of the fibers were treated with TGA using 5% thioglycolic acid at pH 9.3 for 20 min and then the hair was rinsed and shampooed.

Table 4.11 Damage to African American hair by an alkaline relaxer and a reduction relaxer [151]

% Failures during 0–500 cycles of fatiguing		
Treatment	10 g load	30 g load
Untreated	18	50
Alkali relaxed	58	60
TGA (air oxidized)	46	56

4.12.3.3 Damage Comparison Between a Reductive and Alkaline Hair Straightener

The hair used in this study was from a Black male age 31. It had never been treated with chemical or heat treatments. Both of these types of relaxers weaken the hair. During treatment with the alkaline straightener 8% of the fibers broke (during treatment), but for the TGA treatment zero fibers broke suggesting more damage by the alkaline straightener in spite of the fact that a chemical neutralizer was not used after the TGA treatment.

The fatiguing process involves attaching weights to the fibers and then dropping the weights repeatedly to stress the hair analogous to the way it might be stressed by continuous combing. The data shows the greatest distinction between untreated and treated fibers using the lower weights. Therefore this condition is probably the most meaningful indicator of damage to the hair. These data clearly show damage by both straightener treatments; however, greater damage is produced by the alkaline straightener providing 8% vs. 0% failures in the hair treated by the alkaline straightener vs. the reduction straightener simply by stroking the product through the hair and 58% failures vs. 46% failures by fatiguing the hair at the 10 g load see Table 4.11.

Other than the example described in Table 4.11, damage by alkaline straighteners is described only generally in the literature. Nevertheless, alkaline relaxers are among the top consumer complaint products because of hair breakage and alkaline burns. These products are combed through the hair starting near the root ends and combing away from the scalp. However, Wong et al. [123] demonstrated, permanent hair straightening is generally achieved without the application of an external force. So combing an alkaline straightener into the hair is mainly for even distribution of product throughout the hair and not for straightening of the hair per se. After processing, the hair is rinsed carefully with running tap water.

From a chemical perspective of hair damage, we understand what happens during alkaline hair straightening more than we understand the physical implications, however, we do know from the fatiguing experiment by Kamath et al. [151] (Table 4.11) that alkaline straightened African American hair is more brittle and it breaks more readily than un-straightened hair from that same source. We also know that supercontraction of 5–9% [123] occurs during alkaline hair straightening and that straightened hair fibers absorb dye more readily than controls [141], indicative of a more porous fiber and hair damage.

From a chemical perspective, we know that chemical changes occur in the protein regions of all hair structures as well as in the fatty acid regions of the cell membrane complex. Ionization of carboxylic acid and phenolic groups of the amino acid side chains also occurs producing a very negatively charged fiber surface. Alkaline hydrolysis of amide and peptide bonds and beta elimination of cystine are among the many chemical reactions that occur with alkaline hair straighteners. These collective actions allow the unfolding of alpha-helical chains (crystalline

proteins) and reorganization in the filamentous regions to less structured proteins. It would also appear that greater changes occur in the concave part of a curl than in the convex part to allow for permanent straightening to occur. The concave part of a curl being analogous to paracortical cells in wool fiber is higher in cystine rich proteins [152, 153] and contains more cross-links [152, 153] and a higher ratio of matrix to intermediate filaments [154–156]

Hydrolysis of ester and thioester groups of the cell membrane complex occurs at the high pH conditions of alkaline hair straighteners which provides for removal of 18-MEA from the hair surface [157] and weakening of CMC bonding between cuticle and cortical cells. Beyond the delipidation of the fiber surface, the creation of lanthionine residues and loss of crystallinity, few specific reactions have been reported for African type hair after treatment with alkaline straighteners. The lack of more information is most likely from a lack of study. For more on hair damage see the section in Chap. 10 on hair breakage.

4.12.4 Why Alkaline Hair Straighteners Are Permanent and Reductive Are Not But Reductives Provide Some Permanence for Curling

Thibaut et al. [158] studying hair from six persons of Caucasian, North African and African descent found that the hair described as straight had three types of cells arranged in a symmetrical annular arrangement. A core of paracortical type cells were generally surrounded by mesocortical with orthocortical type cells in the outer part of the cortex. However, for high curvature hair the cells were distributed asymmetrically with the orthocortical type cells predominately on the convex side of the curl and the paracortical type cells on the concave side, see Fig. 1.42. Bryson et al. [159] examined curved hair and straight hair from Japanese subjects and found four types of cells rather than three, but found similar distributions to those found by Thibaut et al.

As explained in the previous section, when alkaline straighteners act on curved hair fibers, they cleave disulfide and peptide bonds producing supercontraction of 8–10% and a decrease in crystallinity as shown by X-ray diffraction [141]. To straighten a curl, more contraction must be produced on the convex side of a curl than on the concave side. Therefore more contraction is produced in the paracortical type cells or those containing a higher concentration of cystine [152, 153] and a higher proportion of matrix to intermediate filaments [154–156]. The alkaline straightener also converts some cystine to lanthionine which creates an irreversible situation in that intermediate vicinity.

With a reductive type straightener, no contraction occurs but elongation is produced by combing the hair in the reduced state. However, with no contractive changes in the region of the intermediate filaments and no irreversible bonds being formed such as lanthionine, more mercaptan remains to provide reversible changes

through disulfide-mercaptan interchange. Therefore, permanent straightening is not achieved.

Now when we use the same reductive system to produce a curl there are a few important differences. First and foremost, the hair is relatively straight to begin with. Therefore the arrangement of cortical cell types are in an annular symmetrical fashion as in Fig. 1.42. Secondly, the action of the reducing agent is primarily on the orthocortical type cells which are in the outer regions of the cortex. The third important difference is that when a hair fiber is put into a curled configuration it is stretched on the convex side and compressed or contracted on the concave side of the curl. Apparently these differences, include simultaneous compression and extension as opposed to stretching alone. I conclude that compression allows for more extensive molecular rearrangements analogous to supercontraction to occur primarily in the orthocortical type cells which allows for some degree of permanence to the curvature change compared to similar but not identical changes in the straightening process.

4.13 Depilatories

Most depilatories are of the same basic chemistry as thiol permanent waves and hair straighteners, but are more reactive compositions. These products generally contain thioglycolic acid formulated at a higher pH from 11 to 12.5, and therefore produce a more rapid and more complete reduction of the hair with greater alkaline degradation. See the section described earlier in this Chapter entitled, *Side reactions during the reduction of hair with mercaptans* that describes the reaction of hair with alkaline reagents. More complete reduction with alkaline degradation helps to fulfill the purpose of a depilatory, i.e., to degrade the hair to the point that it can be removed or broken off easily by simply rubbing the area with a washcloth or other device.

Figure 4.1 illustrates the swelling effects of a calcium thioglycolate depilatory on hair. Figures 4.5, 4.6 and 4.7 depict damage induced to the cell membrane complex of different parts of the fiber by reductive treatments. Thus, strong alkaline-reductive treatments degrade the hair proteins to the point where many of these are solubilized in aqueous media.

A very large order swelling occurs with depilatories because of the almost complete reduction of disulfide bonds in the A-layer and the exocuticle of the cuticle and the matrix and intermediate filaments of the cortex and because of the alkaline degradation. The reaction of a depilatory with human hair can be followed nicely with optical microscopy by observing the large order swelling and the loss of birefringence that occurs through the moving boundary kinetics by observing the boundary as it moves rapidly from the periphery of the fiber to the core.

The composition described in Table 4.12 is a thiol type depilatory. This product can be made into either a cream or lotion by controlling the ratio of Part I to Part II. For higher viscosities, a higher ratio of Part I to Part II is used. To make this depilatory described in Table 4.12, disperse the ceteareth-20 into water (part II) by

Table 4.12 Depilatory cream/lotion

Ingredient	Percent
Part I	
Mineral oil	4.5
Ceteareth-20	2.5
Cetearyl alcohol	3.0
Part II	
Water (oxygen free)	q.s.[a]
Part III	
Sodium thioglycolate	3.5
Calcium thioglycolate	3.0
Calcium hydroxide	~1.5 (to pH 11.5)
Fragrance	<1.0

[a]q.s., add water to 100%

heating to 75 . Then add the cetearyl alcohol and mineral oil and continue heating and stirring for about 10 min Cool to 40° while stirring, then add the individual ingredients of Part III and homogenize. Similar precautions as described for the thiol wave such as the exclusion of oxygen and metals from the system must also be exercised for making a thiol depilatory.

Another popular depilatory is the wax type product. This depilatory is applied as a viscous liquid over the hair area to be removed. It is often warmed under the tap prior to application and applied in the direction of hair growth. The wax is sometimes covered with a paper-cloth oftentimes supplied with the product. The cloth adheres to the sticky wax composition on the skin and is pulled in the direction against the hair growth removing much of the sticky wax with the hair. This procedure is repeated until the desired area is depilated. The residual wax is then washed and peeled from the skin.

4.14 Safety Considerations for Permanent Waves

As for other reactive hair products, the primary safety concerns for permanent waves generally arise from misuse or failure to comply with the product's usage instructions. Skin irritation, hair breakage, oral toxicity, sensitization, and scarring alopecia either have been reported in the literature or are referred to in the warning instructions for home permanent-wave products.

A safety assessment of thioglycolic acid by the CTFA [160] summarizes safety data for thioglycolic acid, its salts and esters. Thioglycolates are moderately toxic yet comparable to bisulfite. Sodium thioglycolate has a LD_{50} of 148 mg/kg (i.p. in rats) [161] vs. 115 mg/kg (i.v. in rats) for sodium bisulfite [162].

Thioglycolate waving lotions can irritate skin [163]; however, irritation in home use is rare and may in part be related to the alkalinity of the system [164]. Among the different thioglycolate salts, monoethanolamine thioglycolate is reported to be less irritating to skin than ammonium thioglycolate [165].

Although ammonium thioglycolate has been reported as having a low sensitization potential [166], a few incidents of sensitization have been reported among hairdressers where contact is frequent [166].

Hair breakage and some permanent hair loss have been reported by Bergfeld [167] from misuse of these products, attributed to scarring alopecia. Bergfeld did not specify the extent of hair loss observed; however, he concludes that side effects from home permanent-waving products are minimal if consumers are aware of their hair damage and any inherent skin diseases and if they comply with the product usage instructions [167]. A more recent update on the safety assessment of thioglycolic acid its salts and esters has been published by Burnett et al. [168]. This report included assessment of ammonium thioglycolate, butyl thioglycolate, calcium thioglycolate, ethanolamine thioglycolate, ethyl thioglycolate, glyceryl thioglycolate, isooctyl thioglycolate, isopropyl thioglycolate, magnesium thioglycolate methyl thioglycolate, potassium thioglycolate, sodium thioglycolate and thioglycolic acid. The conclusions of this report are that thioglycolates can be skin irritants in animal and in vitro tests and can also be sensitizing. However, "clinically significant adverse reactions to these ingredients used in depilatories are not commonly seen". Thioglycolates are minimal to severe ocular irritants. They are not mutagenic and show no evidence of carcinogenicity. Similar safety concerns exist for the thiol based hair straighteners.

For alkaline hair relaxers, care must be taken to avoid contact with the scalp to prevent alkaline burns and hair breakage can result from misuse of these products also. Chemical hair straighteners and relaxers are among the top consumer complaint products including complaints of hair breakage, hair damage and scalp burns. While many of these complaints are due to product misuse by either the consumer or a hair stylist, the incidence of complaints are still very high relative to other products.

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Chapter 5
Bleaching and Oxidation of Human Hair

Abstract The physical chemistry of both chemical bleaching and sunlight effects on human hair are described. Recently we have become more aware of the critical involvement of free radical chemistry on both chemical and sunlight oxidative processes for human hair, therefore these effects are included. The beta layers of the cortical lipids with their high density of double bonds with allylic hydrogen atoms are very sensitive to free radical propagation reactions which can degrade the lipids themselves and also lead to protein degradation. Over the past decade our understanding of the biosynthesis and the structures of the melanin pigments has improved greatly; the most current biosynthetic pathway has been added to this Chapter. Initial oxidation reactions remove 18-MEA and free lipids from the surface and between cuticle cells. When metals like iron or copper are present free radical chemistry is increased leading to degradation of lipids and enhanced protein degradation not only at disulfide bonds but even at peptide bonds. Oxidative cleavage of disulfide bonds inside cuticle cells also occurs. Degradation of disulfide bonds inside cortical cells occurs next as well as degradation of hair pigments. Other amino acid functional groups are attacked and oxidatively degraded.

5.1 Introduction

Since the 4th Edition, we have added to our learning about photochemical effects on hair, photoprotection of hair, the surface chemistry of photobleached and chemically bleached hair and the properties of and the biosynthesis of different hair pigments. We have discovered that the beta layers of the cuticle are more sensitive to nucleophilic attack by species such as the hydroperoxide anion and mercaptans, but beta layers of the cortical lipids with their multiplicity of double bonds (oleic plus palmitoleic acids, plus cholesterol and cholesterol sulfate) and tertiary hydrogen atoms (cholesterol and cholesterol sulfate) are more sensitive to free radical chemistry. On the other hand, the proteinaceous membranes of the CMC are resistant to non-radical oxidizing and reducing agents. An expanded

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section in this Chapter deals with free radical chemistry of the important groups in hair and other types of damaging reactions of hair bleaches, oxidation dyes and sunlight degradation. The effects of these reactions on adhesion failure or crack formation in the hair fiber are also described.

A new section entitled *Hair pigmentation and genetics* summarizing the genes and SNP's (single nucleotide polymorphisms) involved in hair pigmentation that control the natural color of human hair has been added in Chap. 3. This current Chapter describes the response of the red hair pigments to photodegradation which differs from that of the brown-black eumelanin. Additional evidence is presented confirming that both photochemical and chemical oxidation of 18-methyl eicosanoic acid (covalently bound lipid on and in the surface) and the disulfide bonds at or near the fiber surface lead to increased levels of sulfur acids primarily as sulfonic acid. The resultant effect creates an acidic, hydrophilic hair surface from a neutral, hydrophobic virgin surface.

Hair pigment size and type are highly important to hair color with the largest pigment particles in black hair and the smallest in blonde hair. Age and geo-racial effects on hair pigmentation are described. Hair pigments, hair dyes, antioxidants and specialty silicones have all been shown to exhibit some effects on photoprotection. These findings are described in this Chapter.

The composition of amino acid residues in bleached hair and in hydrolysates of oxidized keratin fibers is described in Chap. 2 and also in publications by Zahn [1, 2], Robbins et al. [3–6], Maclaren et al. [7, 8], and Alter and Bit-Alkis [9]. Although, several questions remain unanswered with regard to the structures and reactions of hair pigments [10–14], general features of the chemical structure of hair and its reactions with bleach products are best described by the language of physical-organic chemistry.

5.2 Hair-Bleaching Compositions

Cook [15] described hair bleaching compositions several years ago. Complete formulations were listed by Wall in the book edited by Sagarin [16]. The most reliable up-to-date qualitative information on bleaching compositions is found on product ingredient labels. From ingredient labels and the information in this Chapter, hair bleaching compositions can be formulated. Hydrogen peroxide is the principal oxidizing agent used in bleaching compositions, and salts of persulfate are often added as "accelerators" [15]. The pH of these products is generally from 9 to 11. Stabilizers (e.g., sequestrants) and separate containers are often used to reduce the rate of decomposition of the peroxide and to provide satisfactory shelf life.

A maximum hair lightening product for either stripping or frosting hair will generally consist of three different parts, the hair lightener base (alkalinity), the lotion developer (containing the peroxide) and the booster powder or accelerator containing salts of persulfate. The solution applied to the hair will be prepared just prior to use by mixing approximately 50 g of the lightener base with 100 g of the

Table 5.1 Hair lightener base

Ingredient	Percentage
Cocodiethanol amide (standamide KD)	9
Oleic acid	8
Dodecyl benzene sulfonate	7
Neodol 91-2.5	6
Concentrated ammonium hydroxide	6
Sodium sulfate	1
Deionized water	q.s.

Table 5.2 Lotion developer

Ingredient	
Hydrogen peroxide (30%)	17
Dodecyl benzene sulfonate (50%)	16
Nonoxynol-9	6
Cetyl alcohol	3
Stearyl alcohol	2
Phosphoric acid	1
Water	55

Table 5.3 Booster powder (accelerator)

Ingredient	Percentage
Potassium persulfate	27
Sodium silicate	26
Ammonium persulfate	25
Silica	20
Sodium lauryl sulfate	1.8
Disodium EDTA	0.2

lotion developer and two to three packets of the booster powder (approximately 10–12 g in each packet).

To formulate the hair lightener base of Table 5.1, add the amide, the sulfonate and neodol to the water while stirring at room temperature. Add the oleic acid with stirring and then slowly add the alkalinity followed by sodium sulfate.

For the lotion developer of Table 5.2, dissolve the dodecyl benzene sulfonate and nonoxynol-9 in water. Heat to 60°C and add the melted cetyl and stearyl alcohols while stirring. Cool and add the phosphoric acid and hydrogen peroxide (Table 5.3).

For permanent hair dyes even where small shade changes to a lighter color are required, bleaching is also involved. For these systems of permanent dyes, extra peroxide is formulated into the creme developer for the necessary bleaching action. For formulas of this type see the section of Chap. 6 that describes the formulation of permanent hair dyes.

For the spray in the hair lightener of Table 5.4, stir and dissolve the hydroxyethyl cetyldimonium phosphate in water followed by polysorbate-20. Then add the quaternium-80, benzoic acid and disodium EDTA followed by the fragrance.

Table 5.4 Spray in hair lightener

Ingredient	Percentage
Water	q.s.
Hydrogen peroxide (30%)	10
Hydroxyethyl cetyldimonium phosphate	1
Polysorbate-20	1
Quaternium-80	0.5
Benzoic acid	0.3
Disodium EDTA	0.2
Fragrance	0.2

5.3 Reactions of the Proteins of Human Hair with Bleaches

5.3.1 Chemical Oxidation of the Disulfide Bond

The primary purpose in bleaching human hair is to lighten the hair. This goal is most readily accomplished by oxidation. However, because of the severe reaction conditions required for destruction of the chromophoric groups of hair pigments, side reactions with the hair proteins occur simultaneously. Wolfram [12] provided evidence that hydrogen peroxide, the principal component of hair bleach systems, reacts faster with melanin than with hair proteins. However, since hair is primarily proteinaceous it contains a large percentage of oxidizable groups. For example hair contains thioester bonds at the surface and between cuticle cells. Hair also contains disulfide bonds of the cortical matrix and of the cuticle proteins. Because these groups are in the structural proteins of hair, degradation of these proteins also occurs during bleaching.

Chemical bleaching with either alkaline peroxide or alkaline peroxide-persulfate first attacks the thioester groups that bind 18-methyl eicosanoic acid to the surface proteins. This reaction partially removes the hydrophobic surface barrier and it creates sulfur acids (primarily sulfonate groups) on and in the fiber surface. These actions provide an acidic, hydrophilic hair surface with a lower isoelectric point [6, 17–19]. Beard et al. [19] have shown that peroxide alone doesn't oxidize the hair surface, however peroxide with alkali (as in hair bleach compositions) does, but with an induction period. This induction period is reduced or even eliminated by inclusion of small amounts of surfactant in the oxidizing medium. The surfactant most likely removes interfering free lipids from the surface providing access for the nucleophilic hydroperoxide anion to the thioester and disulfide linkages for reaction. When certain metals such as iron or copper or even persulfate are present free radical degradation can also occur. These reactions will be described later in this Chapter.

Chemical bleaches weaken the cell membrane complex by oxidizing thioester between cuticle cells. Bleaches also oxidize cystine residues of the matrix in the cortex and other hair regions rich in cystine such as the A-layer and the exocuticle inside cuticle cells. These reactions result in breakdown of the cell membrane

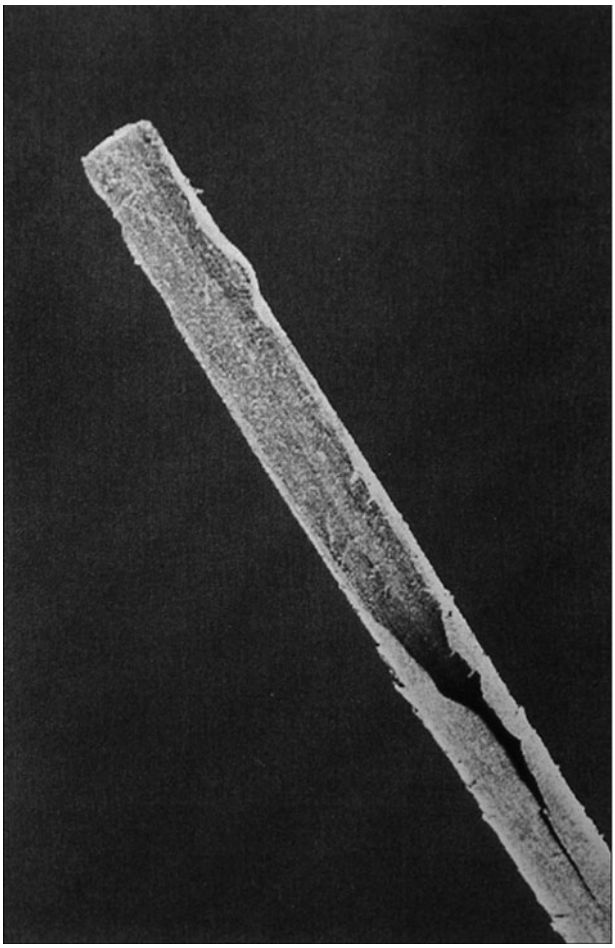


Fig. 5.1 Hair fiber oxidized with alkaline peroxide for a few hours and extended to fracture dry. Much of the cortex has been broken from the interior of the fiber leaving a hollow sleeve of essentially cuticle layers remaining (SEM kindly provided by Sigrid Ruetsch)

complex, the cuticle and cortex components and ultimately dissolves proteins in these regions. The electron micrographs of Figs. 5.1 and 5.2 illustrate the effects of fracturing hydrogen peroxide oxidized hair (extensively oxidized) by extending the treated fibers to break. The cell membrane complex has been weakened by the chemical oxidation as illustrated by the relatively clean breaks between cuticle layers of Fig. 5.2. This effect is illustrated further by the appearance of a hollow cuticular tube with the cortex largely removed (Fig. 5.1). This consequence suggests a relatively clean separation at the cuticle–cortex junction in the cuticle–cortex cell membrane complex. After chemical bleaching there is also a greater tendency for cuticle scale lifting via cell membrane complex failure as illustrated by several electron micrographs in Chap. 6.

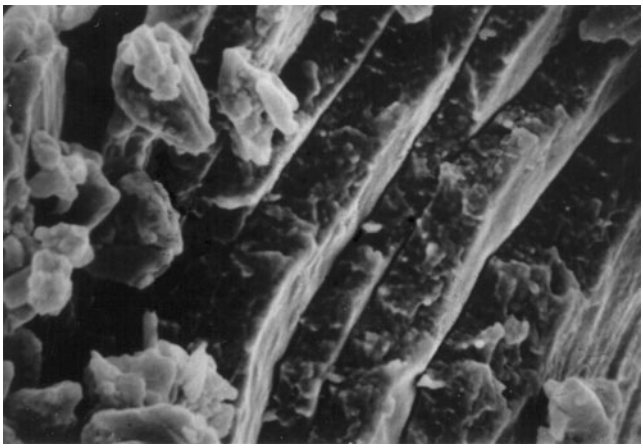


Fig. 5.2 Close up of the fiber in Fig. 5.1 at the main fracture site. Note the clean breaks between the scales at the cell membrane complex (SEM kindly provided by Sigrid Ruetsch)

Zahn [1] first demonstrated that the primary reaction of oxidizing agents with the proteins of human hair occurs at the disulfide bond of cystine. Small amounts of degradation also occur to the amino acid residues of tyrosine, threonine, and methionine during severe bleaching [5]. The main site of attack, however, is at the disulfide bonds of the cystyl residues in the fibers. Robbins and Kelly [5] have shown that 15–25% of the disulfide bonds in human hair are degraded during "normal" bleaching, however, as much as 45% of the cystine bonds may be broken during severe "in practice" bleaching. This latter amount of damage may occur while frosting hair, or while bleaching hair from black or brown-black to light blond.

The kinetics of the oxidation of cystyl residues in hair by hydrogen peroxide has not been reported, although there is evidence to suggest that this reaction is a diffusion-controlled process. Harris and Brown [20] reduced and methylated keratin fibers and demonstrated that the wet tensile properties decrease almost linearly with the disulfide content. Alexander et al. [21] arrived at this same conclusion after oxidizing wool fiber with peracetic acid. Robbins has observed a similar phenomenon for hair oxidized with alkaline hydrogen peroxide. A portion of these data is described in Chap. 9. Therefore, one may conclude that the percentage loss of the wet tensile properties that occurs during bleaching such as the decrease in the 20% index [21] is an estimate of the percentage of cystine linkages that are broken. For a more complete discussion of the effects of bleaching on the tensile properties of hair, see Chap. 9.

Edman and Marti [22] described the change in the 20% index of hair fibers as a function of treatment time in 6% hydrogen peroxide, at 32°C using a 25:1 solution-to-hair ratio at a pH of 9.5. Their data are plotted in Fig. 5.3 vs. the

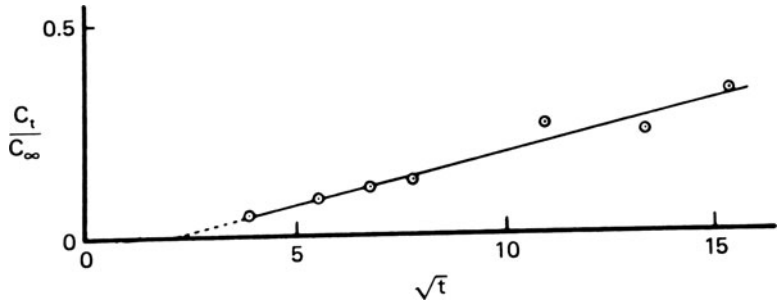


Fig. 5.3 Rate of cleavage of cystine cross links estimated from tensile properties [24] (Reprinted with permission of the Journal of the Society of Cosmetic Chemists)

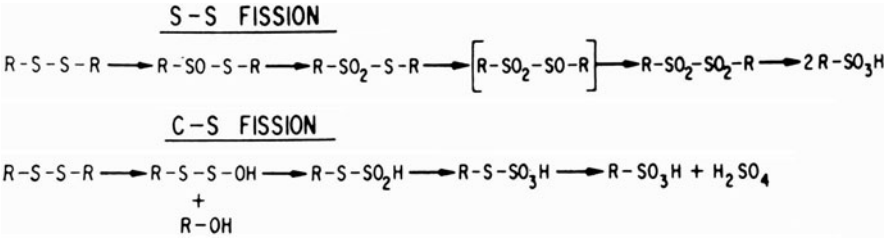


Fig. 5.4 Schemes for disulfide bond fission [24] (Reprinted with permission of the Journal of the Society of Cosmetic Chemists)

square root of time providing a straight line indicative of a diffusion-controlled process. These data have been applied to an equation developed by Crank [23] describing diffusion from a stirred solution of limited volume into a cylinder of infinite length:

$$C_t/C_\infty = 2\left[2/\sqrt{\Pi}(Dt/a^2)^{1/2} + \ldots.\right]$$

The term C_t is the 20% index at time t and represents the amount of cleaved disulfide at time t; C_∞ is the 20% index at time zero representing the total amount of disulfide before oxidation; and a represents the fiber radius, assumed to be 40 μm. Considering these assumptions, one obtains an approximate diffusion coefficient of 1.8×10^{-9} cm^2/min. This diffusion coefficient is of the anticipated magnitude, suggesting that the oxidation of the disulfide bond in hair by alkaline hydrogen peroxide is a diffusion-controlled reaction.

Two schemes have been proposed for the oxidative degradation of disulfide bonds [24, 25]: a sulfur to sulfur (S–S) fission process, and a carbon to sulfur (C–S) fission process see Fig. 5.4.

Table 5.5 Functional groups involved in the oxidation of disulfides and mercaptans

Disulfide oxides	
–S–S–	Disulfide
–SO–S–	Monoxide
$–SO_2–S–$	Dioxide
$–SO_2–SO–$	Trioxide
$–SO_2–SO_2–$	Tetroxide
Sulfur acids	
–SH	Mercaptan
–S–OH	Sulfenic acid
$–SO_2H$	Sulfinic acid
$–SO_3H$	Sulfonic acid

Table 5.5 defines the different functional groups involved in these two oxidative schemes. Figure 5.4 shows that if the oxidation of cystine in hair proceeds totally through S–S fission, then two moles of sulfonic acid should be produced per mole of reacted disulfide. However, if the reaction goes totally through C–S fission, then only 1 mole of sulfonic acid can be produced from each mole of disulfide that reacts. Nachtigal and Robbins [4] have shown that this ratio is greater than 1.6 for frosted hair, suggesting that this reaction occurs largely through the S–S fission route. Secondly, if this reaction occurs through the C–S fission route, the alcohol produced would be a seryl residue and on hydrolysis would produce significantly larger quantities of serine in bleached hair hydrolysates than in hydrolysates of unbleached hair. However, this is not the case because Robbins and Kelly [5] have shown that in samples of hair bleached on heads with commercial bleaching products, the amount of serine remaining is equal to or less than that of unbleached hair. Thus, the oxidative cleavage of the disulfide bond that occurs during the chemical bleaching of human hair by current bleach products is predominately an S–S fission process.

Since chemical bleaching of human hair is carried out in an aqueous alkaline oxidizing medium, hydrolysis of the cystine oxide intermediates (Fig. 5.4) should be competitive with their oxidation. In fact, disproportionation of the cystine oxides [22] may also occur, adding to the complexity of the total reaction scheme; however, the net highest oxidation state of a disulfide under S–S fission conditions is sulfonic acid. This effect is illustrated by the oxidation and hydrolysis reactions of the cystine oxides summarized in Fig. 5.5. Note that disulfide trioxides have never been isolated from oxidized hair. Nevertheless, these species are suggested as "possible intermediates" since both disulfide dioxides and disulfide tetroxides of pure compounds [25] have been isolated by oxidation in an acidic medium. Cystine monoxide and dioxide are sensitive to alkaline hydrolysis [26, 27] but have been isolated from aqueous acidic oxidations [27]. Both the trioxide and tetroxide should be even more sensitive to alkaline hydrolysis than the monoxide and dioxide [25]. Although the importance of hydrolysis relative to oxidation for each of the cystine oxides is not known, it is certain that hydrolysis will be increasingly important with increasing pH. At the pH of current bleach products (pH 9–11) the rate of hydrolysis of these species should be competitive with

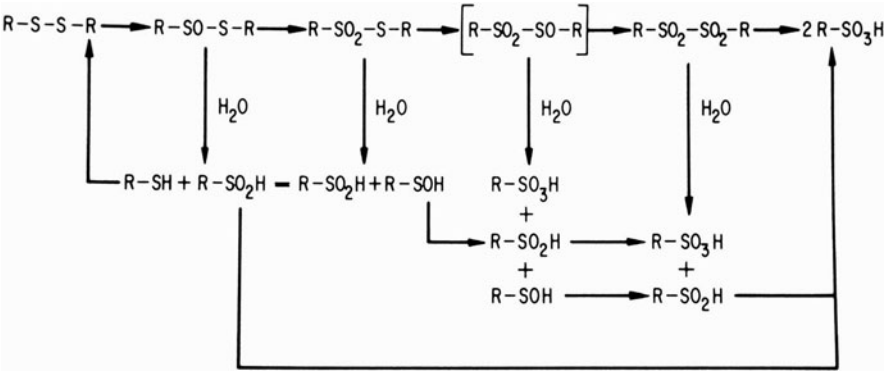


Fig. 5.5 S–S fission of disulfides in an aqueous alkaline oxidizing medium [24] (Reprinted with permission of the Journal of the Society of Cosmetic Chemists)

oxidation, thereby decreasing the probability of existence of these species in major quantities in bleached hair.

Intact hair from bleaching experiments using alkaline hydrogen peroxide and peroxide-persulfate has been examined by both infrared spectroscopy [3, 9] and electron spectroscopy for chemical analysis [6]. Evidence for intermediate oxidation products of cystine (the monoxide through tetroxide) could not be found. However, one cannot conclude that very small quantities of these species do not exist in bleached hair. The primary conclusions from these spectroscopic studies are: (1) the principal end product from the oxidation of cystine during chemical bleaching of hair with either alkaline peroxide or alkaline peroxide-persulfate is cysteic acid, and (2) the cleavage of cystine proceeds primarily through the S–S fission route.

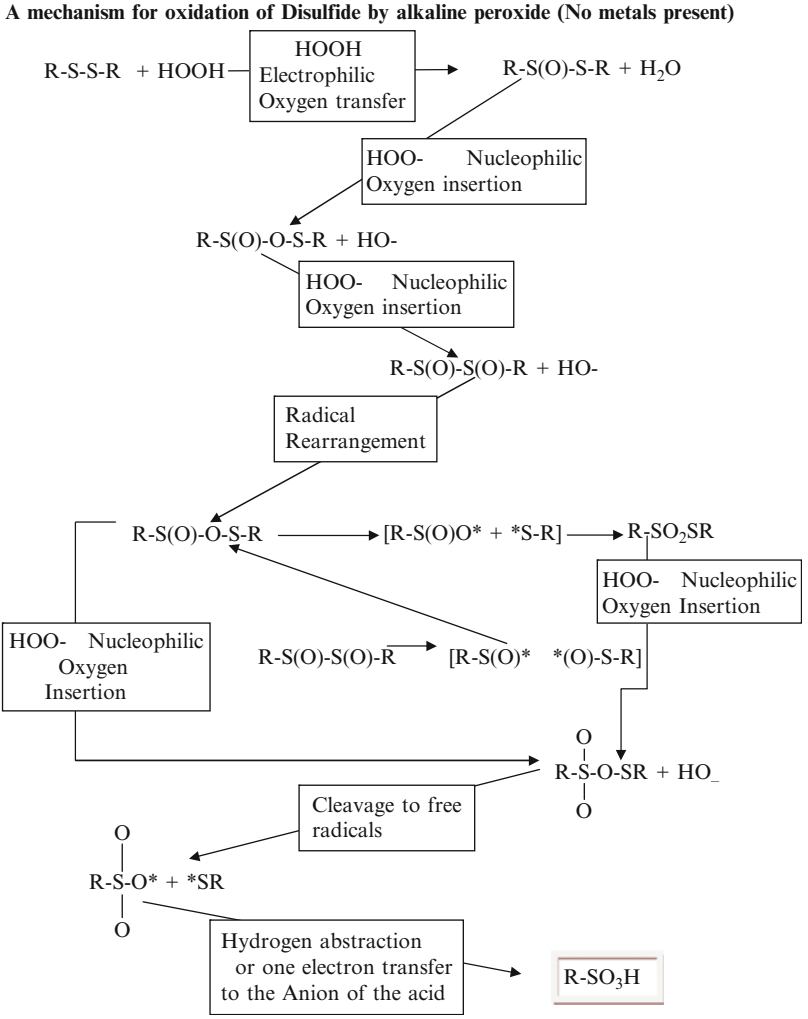
Zahn and co-workers [2], using two-dimensional gel electrophoresis, separated up to 62 isolated protein spots from human hair. From the fluorogram of bleached hair, these scientists identified cystine oxides (monoxide and dioxide). Although, the exact quantities of these intermediate oxidation products vs. cysteic acid were not reported, the quantities were indicated to be small relative to the cysteic acid content [2].

To summarize, sulfonic acid is the principal established end product of the oxidative cleavage of the disulfide bond from the chemical bleaching of human hair with current hair bleach products [3, 9]. The mercaptan content of bleached hair is lower than that of unbleached hair [4]. The intermediate oxidation products of cystine, that is the disulfide monoxide, dioxide, trioxide, and tetroxide do not exist as significant end products of hair bleaching using today's commercial bleach products [3, 6, 9]. Nevertheless, evidence has been presented demonstrating low levels of cystine oxides in bleached hair [2].

Considering all the species from the oxidation of disulfides described in Fig. 5.5, the sulfinic acid is the only species of even moderate stability [28] remaining to be examined. Sulfenic acids are notoriously unstable [29], and disulfide trioxides and disulfide tetroxides are even more sensitive to alkali than are the dioxides and the monoxides. Specific mechanisms for the oxidation of the disulfide bond are described in the next section of this Chapter.

5.3.2 *Proposed Mechanisms for Oxidation of Disulfide Bonds by Alkaline Peroxide*

When virtually no metals are present to generate free radicals, the primary mechanism for oxidation of the disulfide bonds in hair with alkaline hydrogen peroxide occurs through the monoxide and dioxide primarily via electrophilic oxygen transfer and nucleophilic oxygen insertion according to the following pathway through S–S fission. A large part of this mechanism was described to me in a private communication by Dr. Jennifer Marsh:



When metals like iron II or copper I are present hydrogen peroxide can react with these to form free radicals by Fenton's reaction (below) and the oxidation mechanism follows a different pathway but still lead to sulfonate via the S–S fission pathway as summarized below:

Mechanism for the oxidation of disulfide by alkaline peroxide with Metals (Fe++ or Cu+)

$$H_2O_2 + M = HO^{\cdot} + HO^{-} \quad \text{(Fenton Reaction)}$$

$$HO^{\cdot} + \text{R-S-S-R} \rightarrow \text{R-S}^{\cdot}\text{-S}^{+}\text{(OH)-R} \quad \text{(Cation radical)}$$

$$\text{R-S}^{\cdot}\text{-S}^{+}\text{(OH)-R} + O_2^{\cdot -} \rightarrow \text{R-S(O}_2\text{)-S-R} \rightarrow 2\ \text{R-S-O}^{\cdot}$$

$$\text{R-S-O}^{\cdot} + O_2^{\cdot -} \rightarrow \boxed{\text{R-SO}_3^{-}}$$

Marsh et al. [30] described the formation of the hydroxyl and perhydroxyl radicals and molecular oxygen that result in hair by the decomposition of alkaline hydrogen peroxide in the presence of transition metal ions like iron and copper. These free radicals induce formation of cysteic acid from disulfide in the F-layer, and other regions of the fiber during the oxidation dye process when transition metals like copper or iron are present. However, Marsh et al. [30] demonstrated that the inclusion of certain chelants into oxidation dye formulations can inhibit or reduce the formation of cysteic acid at or near the hair fiber surface. These effects are explained by the chelants binding low levels of copper known to be in some tap waters. This action by chelants (in alkaline peroxide) inhibits the known metal induced free radical formation and the resultant formation of sulfonate by the oxidation of disulfide at or near the fiber surface. See Chap. 2 for a description of trace metals found in human hair.

5.3.3 Oxidation of Other Amino Acid Residues

Robbins and Kelly [5] have examined bleached and unaltered hair by hydrolysis and amino acid analysis. Their results for severely bleached hair are summarized in Table 5.6 and suggest that methionine, tyrosine, lysine, and histidine, in addition to cystine, are degraded to the greatest extent (tryptophan could not be evaluated in this study).

These results are consistent with the relative sensitivities of these species to oxidation. Cystine and its reactions with oxidizing agents have already been described. Methionine is also sensitive to oxidation and is probably oxidized to

Table 5.6 The effect of bleaching on the amino acid residues in hair [5]

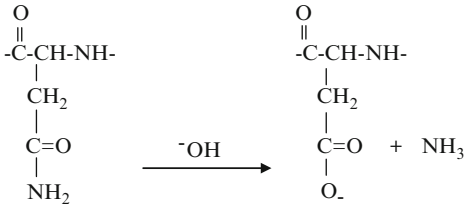
Amino acid	Micromoles/g dry hair		
	Nonfrosted	Frosted	% Difference[a]
Half-cystine	1,509	731	−50
Methionine	50	38	−24
Tyrosine	183	146	−20
Lysine	198	180	−10
Histidine	65	55	−15

[a]Only those amino acids found to be 10% or lower in bleached hair are included in this table

its sulfoxide and possibly to methionine sulfone. Tyrosine, with its electron-rich phenolic ring, is also sensitive to oxidation. The amine salts of lysine and histidine should be resistant to oxidation, although the free amines of these species may be slowly oxidized in the bleach medium.

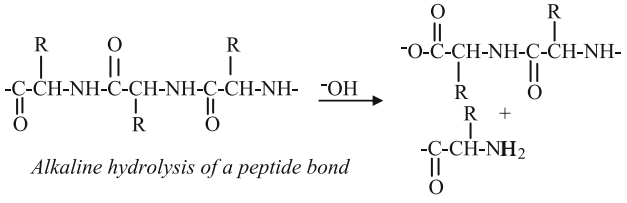
5.3.4 *Hydrolysis or the Action of Alkalinity*

Since bleaching compositions are usually formulated between pH 9 and 11, the hydrolysis of peptide and amide bonds and the formation of lanthionyl residues in hair are possible side reactions during bleaching. The hydrolysis of amide groups of the residues of aspartic and glutamic acids, in addition to the formation of cysteic acid residues, will increase the ratio of acidic to basic groups in the fibers; i.e., amide hydrolysis will decrease the isoelectric and isoionic points of the fibers.



Amide of aspartic acid residue

Peptide bonds are the major repeating structural unit of polypeptides and proteins. Hydrolysis of peptide bonds can occur at high pH and is most likely to occur during frosting or bleaching from black or brown-black to light blond, where long reaction times and higher concentrations of alkalinity and oxidizing agent are employed.



Alkaline hydrolysis of a peptide bond

Harris and Brown [20] have shown that the wet tensile properties of keratin fibers are related to the disulfide bonds, whereas the dry tensile properties are influenced more by peptide bond cleavage [21]. In an examination of frosted hair, Robbins found a 4–8% decrease in the dry tensile properties (see Chap. 9 for details). This suggests that some peptide bond hydrolysis occurs during severe bleaching conditions. Note that the frequency of peptide bonds is nearly an order of magnitude greater than that of the disulfide bonds in human hair.

The formation of lanthionyl residues in alkaline media is described in Chap. 4. Note that if lanthionine is formed during hair bleaching, its sulfoxide and sulfone are also possible oxidation products.

5.3.5 Summary of Chemical Bleaching of Hair Proteins by Peroxide

When hair is exposed to chemical bleaching, changes occur in the surface layers removing some of the 18-methyl eicosanoic acid. Free lipids at the surface and between scales are removed or oxidized. The reaction with 18-MEA results in the formation of acidic sulfur compounds such as mercaptan, sulfinate and sulfonate groups (predominately sulfonate for chemically bleached hair). A decrease in the free lipid content in the surface layers also results which with removal of 18-MEA provides a dry feel to the hair. These changes convert the virgin hair fiber and especially the surface from a hydrophobic, entity with little surface charge to a more hydrophilic, more polar and more negatively charged surface; see Chap. 6 for additional details. In addition, cystine degradation occurs in the cystine rich A-layer and the exocuticle of the cuticle. Tensile data clearly shows that cystine degradation occurs in the matrix and intermediate filaments of the cortex too. In addition, methionine, tyrosine, histidine and lysine are modified by oxidation and some of the peptide and amide groups are hydrolyzed by alkaline degradation.

5.4 Oxidation of Hair Proteins and the Cell Membrane Complex by Sun and UV Light

Light radiation attacks hair proteins of the cuticle and the cortex, in addition to the cell membrane complex lipids (attached to the cell membrane proteins) and the hair pigments. The emphasis in this section is on the photochemical degradation of the proteins and lipoproteins of hair with special emphasis on the cell membrane complex lipids and proteins. Later in this chapter, in the discussion on hair pigments, the effects of light radiation on melanins are considered.

Unfortunately, many of the published manuscripts dealing with photochemical degradation employ different units of radiation or widely varying exposures making

comparisons difficult. Signori [31] suggested that comparisons be made in terms of total irradiation energy using units of J m^{-2} $month^{-1}$ (Joules per meter squared per month). A typical Florida Month of exposure provides 295 $\times$ 10^6 J m^{-2} $month^{-1}$ of UV plus visible light and 25 $\times$ 10^6 J m^{-2} $month^{-1}$ of UV light. Many photochemical treatments of hair in the literature are well beyond this level of exposure. However, 1–4 Florida months of exposure appears to be a reasonable high level of exposure that might occur on the hair of Florida sunbathers.

The covalently bound lipids of the CMC of the cuticle are sensitive to oxidation, reduction and to alcoholic alkalinity while the lipid Beta layers of the cortex are affected more by lipid solvents and free radical chemistry. For example, the Beta layers of the cuticle are more sensitive to nucleophilic attack by species such as the hydroperoxide anion and mercaptans, but the Beta layers of the cortex with their multiplicity of double bonds (oleic plus palmitoleic acids, plus cholesterol and cholesterol sulfate) and tertiary hydrogen atoms (cholesterol and cholesterol sulfate) are more sensitive to free radical chemistry. On the other hand, the membranes of the CMC are resistant to oxidizing and reducing agents [32]. Several of these chemical actions make the CMC more vulnerable to fracture, to cuticle fragmentation and to the propagation of cracks through the cortex leading to split hairs.

There is evidence that an appreciable amount of free-lipid (not covalently bound to hair proteins) is in the Beta layers of the cuticle and likely in all lipid layers of keratin fibers [33]. Furthermore, about 50% of free-lipid in human hair is fatty acid and free lipid provides acidic groups to the hair surface and decreases the isoelectric point as shown by Capablanca and Watt [34] for wool fiber. As hair is exposed to repeated shampooing, blow drying, rubbing and to sunlight, changes occur on and in the surface layers. These changes involve removal of some free lipids by shampoos, photo-degradation of 18-MEA, disulfide and other functional groups. Consequently, the fiber so weakened can form fractures in or between layers from severe bending, stretching and abrasive actions during combing and/or brushing.

These actions expose “new” protein material and sulfur acids primarily sulfonate groups with an accompanying decrease in the free and bound lipid content of the hair surface. In that manner, the virgin hair surface is converted from a hydrophobic entity with little surface charge to a hydrophilic, polar and negatively charged surface. The more exposure of the hair to chemical and abrasive actions, such as the further from the root ends the more hydrophilic, more polar and more negatively charged the surface becomes.

5.4.1 Damage by Shampoos and Conditioners and Irradiation

The dissolution or the removal of structural lipids or proteinaceous matter from hair, primarily from the CMC or endocuticle, by shaking keratin fibers either in surfactant or shampoo solutions or even water has been demonstrated by several different scientists. For example, Marshall and Ley [35] demonstrated the extraction of proteinaceous components from the cuticle of wool fiber by shaking it in

sodium dodecyl sulfate solution, a common surfactant in many shampoos. Gould and Sneath [36] examined root and tip end sections of scalp hair by TEM and observed holes or vacancies in thin cross-sections of the hair. This hair had never been chemically treated. These holes were more frequent and larger in tip ends than in root ends. These scientists attributed these holes to damaging effects by shampooing and weathering involving the breakdown and removal of the non-keratin portions (CMC and endocuticle) of the hair leaving the intercellular regions more susceptible to fracture under stress. It is likely that sun exposure helped to make the hair more vulnerable to the actions of shampoos; however sunlight effects were not examined in this study.

Beta-delta failure [37] is one of the most common types of fractures in hair fibers. This fracture occurs in the cuticle–cuticle CMC between the upper Beta layer and the adjoining Delta layer (see Fig. 6.31) and it occurs most readily when the fiber is dry. Gamez-Garcia [38] noted that the lower the relative humidity or the moisture content of hair, the lower the strain level required to produce Beta-delta failure.

Beta-delta failure was observed by Negri et al. [37] on wool fiber who noted disruption of the cuticle–cuticle CMC along the upper Beta layer in TEM sections. With this type of fracture, the Delta layer and the lower Beta layer are both retained on the underside of the "old" outermost cuticle cell. As a result 18-MEA is left as the "new" hair surface once the "old" outermost cuticle cell is abraded away. This type of fragmentation has been described in detail by Feughelman and Willis [39] who proposed that the failure of adhesion between overlapping scales involves 18-MEA. Furthermore, the chain branch in 18-MEA provides mobility and a reduction in adhesion between scales leading to Beta-delta failure. Therefore, chemical degradation of 18-MEA, both on the surface and between scales leads to further weakening of this structure and more rapid Beta-delta failure leading to faster cuticle fragmentation and cuticle loss. Ruetsch and Kamath [17] have shown that 18-MEA is degraded by chemical and photochemical bleaching. Ruetsch et al. [40] has shown that it is degraded by alkalinity and Robbins [41] has shown that it is degraded by permanent wave treatments.

5.4.2 Wet Versus Dry State Failure and Oxidative Exposure

Deformations such as stretching as shown by Robbins [42] and by Kamath and Weigmann [43] (including extension cycling by Gamez-Garcia [38]), bending as in a snag or a knot [42, 44] or twisting in the wet state are very different than deformations in the dry state. This is because failure in the wet state generally involves fractures or breaking bonds in hydrophilic layers, such as the endocuticle or the central contact zone of the CMC. In contrast, failure in the dry state generally involves fractures in or between hydrophobic layers, e.g., Beta-delta failure [39, 42]. Failure in the wet state generally involves hydrophilic regions because when a layer or region is completely swollen less mechanical stress is required to distort that layer

and to produce a fracture. At low relative humidity or swelling condition of a hydrophilic layer, more mechanical stress is required to distort it relative to hydrophobic layers and therefore fractures are generally produced in hydrophobic layers.

Extension of undamaged hair to break generally produces smooth fractures [44]. However, as the hair becomes more damaged or as the relative humidity is decreased and especially at lower humidity more step fractures are produced [43]. Step fractures involve extensive fracturing in the cortex–cortex CMC, most likely in the lipid or Beta layers. Kamath and Weigmann [43] demonstrated at low moisture content, crack initiation occurs most often in the cortex. However, at high moisture content, fractures almost always initiate at or near the fiber surface because of the high pressure of the swollen cortex against the cuticle.

Step fractures involve the axial propagation of cracks either through the cortex–cortex CMC (see Fig. 1.45) or the medulla [43] and because these regions are hydrophobic they tend to occur more frequently in the dry state than when hair fibers are wet [43]. Kamath and Weigmann [43] also concluded that, the CMC seems to "play an important role in stress transfer and axial splitting" of human hair fibers.

The abrasion resistance of human hair is decreased by most chemical treatments including photo-oxidation as shown by the "Protein loss" test of Sandhu and Robbins [45] or by the release of labile and eluted proteins as described by Inoue et al. [46]. These tests are both wet state methods. The interior of cortical cells is degraded by alkaline peroxide, thereby weakening the cuticle and cortex cells internally. Alkaline peroxide degrades the cuticle–cuticle CMC weakening the cellular cohesion or the resistance of scales to break apart. Cuticle fragmentation in the dry state is caused primarily by the rupture between cuticle cells through Beta-delta failure [38, 39] and the resultant chipping of cuticle from the hair via abrasive actions. Cuticle loss in the wet state is primarily caused by rupturing of cuticle cells internally and is greater in chemically damaged hair such as alkaline peroxide treated, permanent waved or irradiated hair than in chemically untreated hair. This type of cuticle loss is due to the decrease in disulfide crosslinks and an increase in hydrophilic sulfonate groups [45].

Fatigue testing a method developed at TRI-Princeton by Ruetsch, Kamath and Weigmann (involves attaching a weight to a hair and dropping the weight multiple times to continuously shock or jar the fiber) shows that alkaline peroxide treatment of human hair fibers when fatigued produces numerous scale edge fractures with scale edge chipping. Ruetsch [47] fatigue tested peroxide treated hair in the dry state followed by stretching and found extensive fracturing in the CMC between the scales due to a weakened cuticle–cuticle CMC by oxidative treatments, chemical or simulated sunlight. This effect is most likely due to oxidative attack on thioester linkages that disrupts the Beta layers of the cuticle–cuticle CMC.

Takahashi et al. [48] provided evidence that wet cuticle wear in Asian hair is due more to CMC failure (possibly involving the central hydrophilic "contact zone" of the Delta layer) rather than failure inside cuticle cells as in Caucasian hair (most likely endocuticular failure). Takahashi et al. [48] showed that wet cuticle wear on Asian hair occurs at a faster rate than on Caucasian hair. This increased wet cuticle

wear is because of differences between Asian and Caucasian hair in the elasticity of the different layers inside cuticle scales. Takahashi et al. showed that the scales of Asian hair are removed faster by wet sonication after extension to 35% or by bleaching the hair followed by shampooing and wet combing the hair over a large number of cycles. In the latter case after 90 grooming strokes for four cycles fewer scales were found on Asian hair relative to Caucasian hair (1.3 vs. 3.2 scales respectively).

On further examination of the hair using an Atomic Force Microscopic probe these scientists found a greater difference in elasticity as a function of depth for the Caucasian vs. Asian hair (1.41 vs. 1.26). Therefore, Takahashi et al. concluded that the scales of Asian hair are removed more by fracturing in the cuticle–cuticle CMC (even in the wet state) while the scales of Caucasian hair fractures inside the scales most likely in the swollen endocuticle. It is interesting to note here that Nakamura [49] by staining reactions has concluded that the composition of the proteins of the Delta layer of the cuticle–cuticle CMC is very much like that of the very hydrophilic endocuticle.

5.4.3 CMC Lipids Degraded by Both UV and Visible Light

Hoting and Zimmerman [50] studied radiation damage to hair as a function of wavelength and determined that the CMC lipids of hair fibers are degraded most by visible light, but also by UV-A and UV-B light. These results help to explain the weakened CMC (of cuticle and cortex) and the multiple step fractures that result from the axial propagation of cracks through the cortex–cortex CMC in sunlight oxidized hair. Furthermore, Hoting and Zimmermann demonstrated that cystine, proline and valine are degraded more in light brown hair than in black hair confirming that the photo-protective effect by hair pigments is stronger in dark hair than in light hair.

Korner et al. concluded that one weak link to photo-chemical attack on lipid structures in the cuticle CMC are the tertiary hydrogen atoms of 18-MEA [51]. Cholesterol and cholesterol sulfate also contain tertiary hydrogen atoms and should provide sites for hydrogen abstraction in photo-chemical reactions. In addition, the allylic hydrogen atoms of oleic and palmitoleic acids and of cholesterol and cholesterol sulfate in the cortex–cortex CMC are especially vulnerable to photo-oxidative reactions as described later in this Chapter.

Long term irradiation does not provide for clean breaks between structural components of human hair as was observed for peroxide oxidized hair. However, long term radiation leads to cross-linking or fusion reactions similar to long term radiation on wool fiber as explained in the next section of this Chapter. For hair damaged by sunlight, in some cases, the lipids of the cuticle CMC appear altered to a greater extent than the more susceptible areas of the cortex CMC because the outer layers of the fiber receive higher intensities of radiation.

5.4.4 *Short Term Irradiation Attacks CMC Lipids Producing Internal Step Fractures*

Fracturing of wool fiber exposed to simulated sunlight has been studied microscopically by Zimmermann and Hocker [52]. Electron micrographs of human hair fibers exposed to simulated sunlight and then fractured were provided to this author by Sigrid Ruetsch showing that human hair provides similar effects to wool fiber. Zimmerman and Hocker demonstrated that stretching non-irradiated control wool fibers in water provided primarily smooth fractures, while short and intermediate times of simulated sunlight exposure caused the fibers to break mainly as step fractures. These scientists suggested that short and intermediate-term irradiation damages the lipids of the CMC (all three types of CMC) and thereby provides many internal step type fractures by axial propagation of cracks through the photochemically damaged cortex CMC.

5.4.5 *Long Term Irradiation Produces Fusion Reactions Across Structural Boundaries*

Longer term irradiation creates cross-links in the fibers fusing the hair across structural boundaries creating amorphous fractures. Cracks do not occur between structural boundaries as in less damaged hair, but clean smooth fractures across cuticle and outer cortex boundaries see Figs. 5.6, 5.7, 5.8 and 5.9. Figures 5.10, 5.11 and 5.12 show the effects of ultraviolet exposure followed by reaction with alkaline hydrogen peroxide for different times (15 min to 2 h). The effects of alkaline

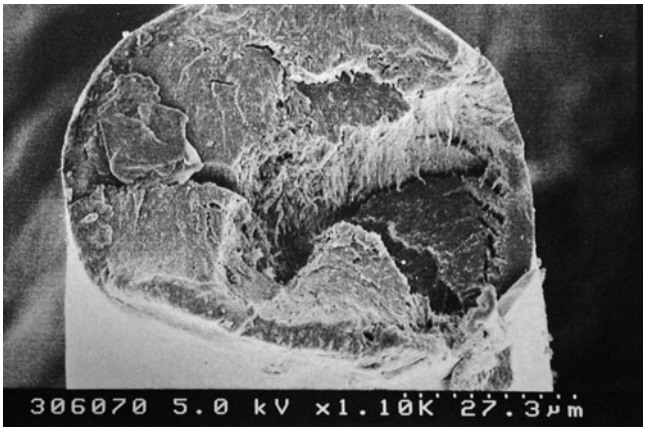


Fig. 5.6 Hair fiber exposed to ultraviolet radiation and extended to break dry (SEM was taken at the fracture site and kindly provided by Sigrid Ruetsch)

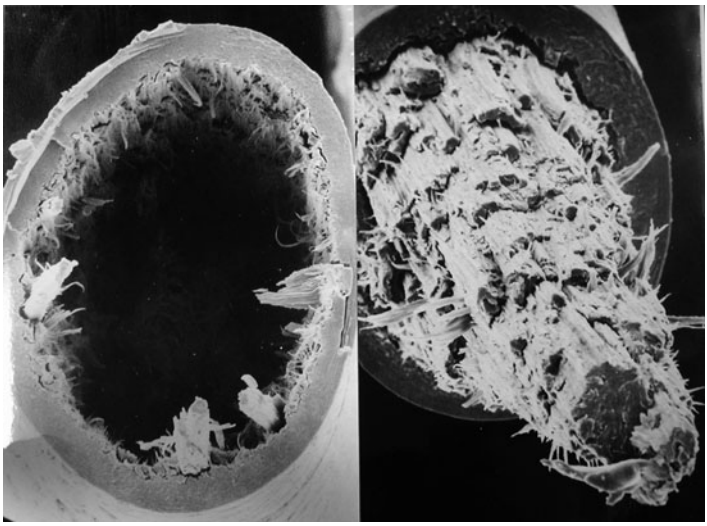


Fig. 5.7 Another hair fiber exposed to ultraviolet radiation and extended to break. SEM's were taken at the fracture site. *Top*: shows a sphire-like break containing multiple step fractures that broke away from the *Bottom*: leaving a hollow cavity in the hair (Micrographs kindly provided by Sigrid Ruetsch)

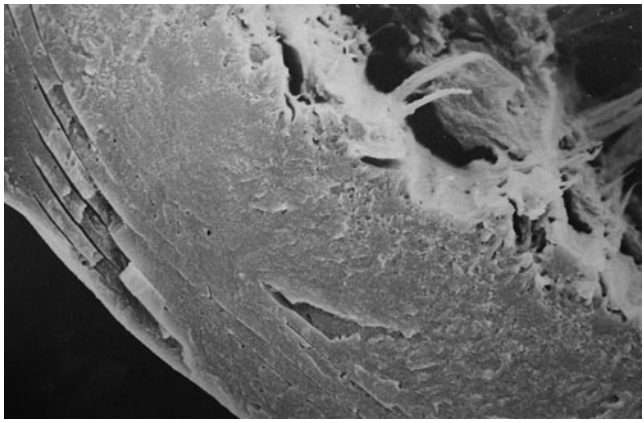


Fig. 5.8 High magnification of the periphery of the fiber in Fig. 5.7. Note the diminished definition of cuticle layers indicative of fusion reactions (SEM kindly provided by Sigrid Ruetsch)

peroxide on hair after long term exposure to ultraviolet are to fuse and then dissolve parts of the cuticle providing for even less structural differentiation. Part of the cuticular proteins are solubilized by these combined chemical treatments into gelatin-like glue that is re-deposited between the fibers, see Fig. 5.11. This effect was produced after only 15 min exposure to alkaline peroxide after long term photochemical degradation. The total lack of surface structural definition is seen

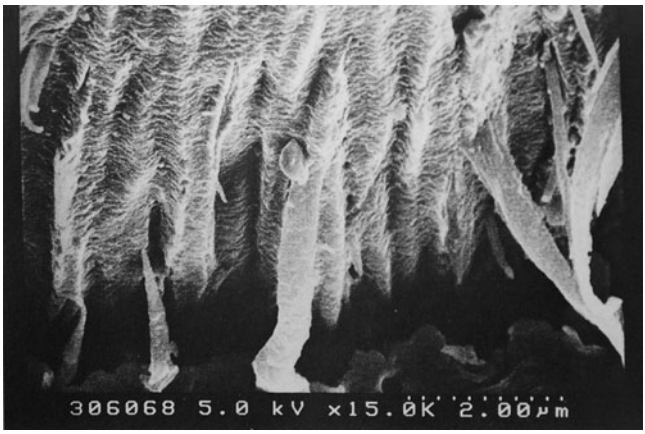


Fig. 5.9 High magnification view of the cortex of the UV exposed-fractured fiber of Fig. 5.6. Note the fusion occurring between cortical cells (SEM kindly provided by Sigrid Ruetsch)

Fig. 5.10 Hair fiber exposed to ultraviolet radiation and then bleached for 15 min with alkaline peroxide. Note the decreased scale definition (SEM kindly provided by Sigrid Ruetsch)

in the most extreme case in Fig. 5.12 where no cuticle scale definition exists after long time ultraviolet exposure and 2 h with alkaline peroxide. This lack of scale definition is probably due to the combined dissolution of the cuticle and the re-deposition of proteinaceous material onto the surface, thereby, masking the scales as occurs in the peracid treatment described later in this Chapter.

Zimmermann and Hocker [52] demonstrated that short and intermediate term radiation attacks CMC lipids providing for increased Beta-delta failure in the cuticle–cuticle CMC and multiple step fractures in the cortex CMC. Longer term irradiation produces amorphous fractures by fusion reactions through the creation of carbonyl groups that are cross-linked through lysine, analogous to the oxidative damage to proteins and mitochondrial decay associated with aging described by

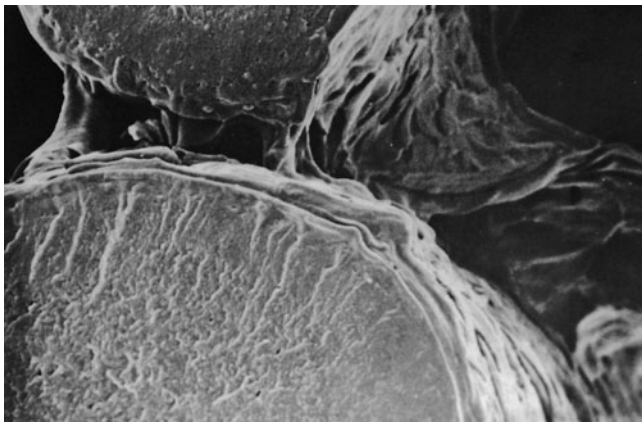


Fig. 5.11 Hair fibers exposed to ultraviolet light and then bleached with alkaline peroxide for 4 h. Note the decreased scale differentiation and the apparent "glueing" together of the fibers by the "gelatinized" hair proteins (SEM kindly provided by Sigrid Ruetsch)

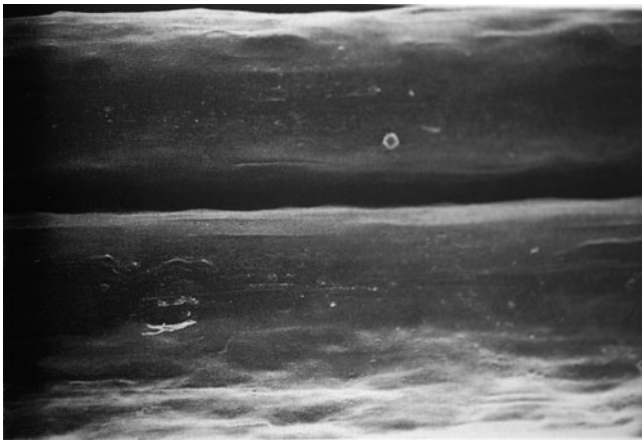
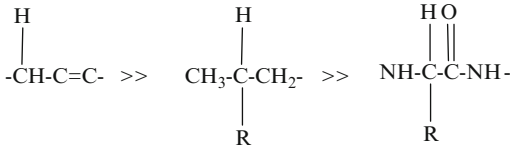


Fig. 5.12 Hair fibers exposed to ultraviolet radiation and bleached with alkaline peroxide for 2 h. Note the total lack of scale definition (SEM kindly provided by Sigrid Ruetsch)

Dean et al. [53]. These fusion reactions start in the periphery of the fiber where it receives higher intensities of radiation than the core, providing a smooth fracture at the periphery and multiple step fractures in the interior of the fibers (Figs. 5.7 and 5.8). If the fibers are exposed long enough to light radiation, amorphous fractures are produced across the entire fiber.

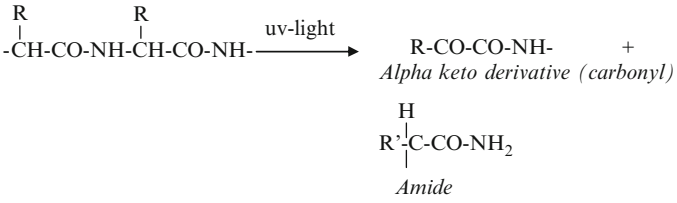
Short and intermediate term exposures to radiation are propagated by abstraction of hydrogen atoms from tertiary carbon atoms of 18-MEA [51] and of allylic hydrogen atoms of oleic and palmitoleic acids in lipids of the cuticle CMC. The cortex-CMC contains tertiary hydrogen atoms on cholesterol and cholesterol sulfate and allylic hydrogen atoms on oleic and palmitoleic acids, and on cholesterol and

cholesterol sulfate that react similarly. The abstraction of hydrogen atoms from tertiary carbon atoms on amino acid side chains (analogous to the tertiary carbon atoms on 18-MEA and cholesterols) has been shown by Goshe et al. [54] to predominate over the abstraction of hydrogen atoms at the alpha carbon atom of amino acids in poly-peptides. However, the abstraction of hydrogen atoms at allylic positions should be even faster.



Allylic Tertiary hydrogen atom Tertiary hydrogen at α-carbon

These facts help to explain why the Beta layers are degraded faster by photo-oxidation than the hair proteins. Photochemical reactions in the Beta layers on allylic groups are very fast and lead to axial failure including splitting. However, photochemical reactions in the proteins are slower leading to cross-linking (fusion reactions) and amorphous fractures.

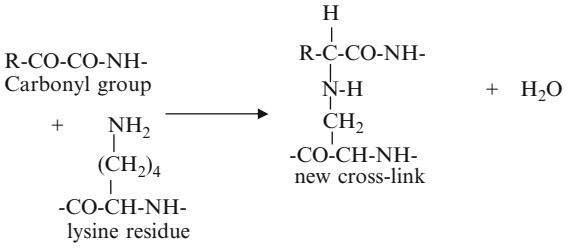


Rupture of peptide bonds by uv light

Oxidation at the peptide backbone carbon has been shown to occur from ultraviolet exposure both in wool [55] and in hair [6], producing carbonyl groups (alpha keto acid/amide) and amide groups. Ultimately these reactions can lead to new cross-links as described in the equations below. The formation of carbonyl groups is favored in the dry state reaction more than the wet state. This reaction has been documented using infrared spectroscopy by Robbins [3] and Dubief [18].

Figures 5.6, 5.7, 5.8 and 5.9 (described earlier) illustrate hair fibers exposed extensively to simulated sunlight and extended to break. These SEM's show that long term ultraviolet exposure causes severe chemical degradation to the hair proteins. As indicated above, the damage is so extensive that structural differentiation is diminished. This physicochemical degradation usually occurs at a higher level in the hair fiber periphery with a gradient to a lower level of oxidative damage deeper into the fiber. Such damage leads to unusual fracture patterns during extension, see Figs. 5.7, 5.8 and 5.9. The breakdown of disulfide bridges within structural units of the A-layer and the exocuticle and matrix and the establishment of new intra- and intermolecular cross-links via reaction of carbonyl groups with protein amino groups (see reactions described below) within and between

structural units decreases structural definition. These reactions collectively lead to a fusion of different structures and a gradual increase in brittleness accompanied by a loss of structural differentiation as shown in these photomicrographs (Figs. 5.7, 5.8 and 5.9).



Formation of cross-links from rupture of peptide bonds by uv light

Subsequent exposure to aqueous alkaline solution or to alkaline peroxide solutions leads to rapid dissolution of the affected areas (Figs. 5.10 and 5.11). Longer exposure of these ultraviolet radiated fibers with oxidizing solutions leads to dissolution/ elimination of scale differentiation and dissolution of the melanin granules, see Fig. 5.12.

5.4.6 Fusion Reactions at Peptide Bonds from Free Radicals at Alpha Carbon Atoms

The fusion reactions of wool and human hair (described above) are believed to be related to the oxidative damage of proteins and mitochondrial decay associated with aging described by Dean et al. [53] and are believed to involve the abstraction of a hydrogen atom from the alpha carbon of an amino acid residue in a protein chain in a keratin fiber [56] which can then either add oxygen to form a hydroperoxide or lose hydrogen to form a dehydropeptide. Meybeck and Meybeck [56] concluded that either route forms an alpha-keto acid (carbonyl group) after hydrolysis. This effect results by cleaving the protein chain to form the alpha-keto acid and a primary amide. The alpha-keto acid then reacts with a lysine residue to form a new amide cross-link in the fibers and thus the fusion reaction is completed.

Carbonyl groups have been shown to be formed by irradiation of wool with simulated sunlight and this reaction is related to photoyellowing of keratin fibers. Holt and Milligan [55] identified keto acids (carbonyl groups) in irradiated wool by reductive amination with sodium ^{3}H-borohydride in ammonia. This reaction converts keto acids to the corresponding ^{3}H-amino acids. By this type of labeling, Holt and Milligan demonstrated that by irradiating wool, carbonyl groups are formed from alanine, glycine, proline, serine, threonine, glutamic acid and tyrosine. Therefore, free radicals were formed from these amino acids by hydrogen atom abstraction at the alpha carbon atom.

However, as indicated earlier, the fusion reactions are slower than the other free radical reactions involving hydrogen atom abstraction, because the abstraction of hydrogen atoms from tertiary carbon atoms of side chains of amino acid residues has been shown to be prevalent over the abstraction of hydrogen atoms alpha to the peptide function [54] and the abstraction of a hydrogen atom from an allylic group is even faster. Furthermore, the consequences of the fusion reactions appear only after the most intense and longest radiation times on wool fiber as shown by Zimmermann and Hocker [52].

5.4.7 *Photoprotection by an Oxidation Dye*

Hoting and Zimmermann [50] demonstrated that the CMC lipids of the cortex of hair, previously bleached with peroxide-persulfate, are more readily degraded by radiation than the lipids of chemically unaltered hair or the lipids of hair dyed with a red oxidation dye. This conclusion was reached by analysis of the cholesterol containing lipids of hair which reside primarily in the cortex CMC. Peroxide-persulfate oxidation of hair is primarily a free radical oxidative process and it leaves hydroperoxide groups in the hair in the CMC and in other regions.

Thus the action of sunlight on peroxide-persulfate bleached hair (containing hydroperoxides) makes the hair more vulnerable to cuticle fragmentation and to splitting that the CMC plays a significant role in. In this same paper these scientists demonstrated that one red oxidation dye provides photo-protection to both UV-A and visible light but not to UV-B light. Hair when treated with this red dye when compared to chemically untreated hair retards the degradation of the CMC lipids most likely by the dye acting as a radical scavenger.

5.4.8 *Other Physical Effects from Photochemical Reactions with Hair*

Beyak [57] and Dubief [18] demonstrated that sunlight and ultraviolet light decrease the wet tensile properties of human hair. Beyak related these effects to the total radiation that the hair is exposed to, rather than to any specific wavelength. However, more recently, hair protein degradation by light radiation has been shown to occur primarily in the wavelength region of 254–400 nm. Hair proteins have been shown by Arnaud et al. [58] to absorb light primarily between 254 and 350 nm.

Dubief also determined that swelling of photochemically damaged hair is increased relative to undamaged control hair. This effect was demonstrated by both the alkali solubility test [18, 59] and by swelling in sodium hydroxide [18].

Several amino acids of hair absorb light in this region (254–350 nm). Therefore, these amino acids are the most subject to degradation by light. The following amino

acids have been shown to be degraded by weathering actions (primarily light radiation) on wool fiber by Launer [60] and by Inglis and Lennox [61]; cystine and methionine (two sulfur-containing amino acids); the aromatic and ring amino acids—phenylalanine and tryptophan (often associated with photo-yellowing of wool), histidine, and proline; and the aliphatic amino acid leucine.

Pande and Jachowicz [62] used fluorescence spectroscopy to monitor the decomposition of tryptophan in hair. These scientists demonstrated that photodegradation of tryptophan occurs in hair. In addition, they speculated that photodamage to tryptophan can increase the sensitivity of other amino acids to photodegradation as explained in the section of this Chapter entitled, *Mechanisms for photochemical reactions in human hair*.

5.4.9 Other Photochemical Reactions with Hair Fibers

Robbins and Kelly [63] analyzed amino acids of both proximal and distal ends of human hair and demonstrated significantly more cysteic acid in tip ends. They attribute this change to weathering actions, specifically to ultraviolet radiation attack on disulfide and thioester bonds. This same study also found significant decreases in tip ends for tyrosine and histidine similar to the weathering effects in wool fiber. Decreases were also reported in the lysine content in this study on hair weathering. This effect could be from the cross-linking reaction of lysine with carbonyl groups formed by ultraviolet attack on peptide bonds (described above).

Robbins and Bahl [6] examined the effects of sunlight and ultraviolet radiation on disulfide sulfur in hair via electron spectroscopy for chemical analysis (ESCA) [6]. Both UV-A (320–400 nm) and UV-B (290–320 nm) radiation were shown to oxidize sulfur in hair. The primary oxidation occurs closer to the hair fiber surface, probably from attack on thioester and disulfide, producing a steep gradient of oxidized to less oxidized hair from the outer circumference of the hair to the fiber core.

The ESCA binding energy spectra (S 2p sulfur) for weathered hair and hair exposed to an ultraviolet lamp in the laboratory are similar but differ from spectra of chemically bleached hair (alkaline hydrogen peroxide). Similar binding energies suggest similar end products and similar mechanisms of oxidation. As described earlier in this chapter, the mechanism for peroxide oxidation of pure disulfides and for disulfide residues in hair is believed to proceed through the S–S fission route. On the other hand, for irradiation of pure cystine, existing evidence by Savige and Maclaren [25] suggests the C–S fission route as the preferred route for photochemical degradation of cystine and for other pure disulfides (see Fig. 5.4). For the photochemical reaction, if the pH is neutral or alkaline, then the C–S fission route is the preferred one; however, if the pH is acidic, then the homolytic or S–S fission route is more likely to occur.

The evidence from ESCA suggests that both the chemical and the photochemical degradation of cystine in hair are similar to that of pure disulfides [6], that is, for chemical degradation, S–S fission occurs, while for photochemical degradation the,

C–S fission route is the preferred route. For the S–S fission route, the main end product is sulfonic acid. For the C–S fission route, the main products are the S-sulfonic and sulfonic acids [25]. However, ultimately, S-sulfonic acid is degraded by light to sulfonic acid [25]. The ESCA spectra suggest that cystine S-sulfonate and cysteic acid are both formed in weathered (tip) ends of hair and in hair exposed to ultraviolet light. But, cysteic acid is the primary end product formed from the oxidation of cystine in hair during chemical bleaching [6]. These results suggest that the mechanism for the radiation-induced degradation of cystine occurs through the C–S fission pathway and is different from the chemical oxidation of cystine that proceeds mainly via the S–S fission route.

Tolgyesi [64] and Ratnapandian et al. [65] proposed a homolytic scission of the disulfide bond by sunlight; however this mechanism ignores the resultant end products of the reaction. It is likely that the photochemical reaction is not as clean as that of the chemical route. Therefore, both pathways are possible and likely to occur when the reaction is photochemically induced. Nevertheless, the formation of cystine S-sulfonic acid cannot be explained by the homolytic scission of the disulfide bond alone. Mechanisms for both hemolytic scission and C–S scission will be described in the next sections of this Chapter.

5.4.10 Summary of Sunlight Oxidation of Hair Proteins

As hair is exposed to sunlight changes occur by removal of 18-MEA at the surface and between scales by the free radical oxidation of sulfur compounds forming mercaptan, sulfinate and sulfonate groups (primarily sulfonate) and a decrease in the free lipid content in the surface layers. These changes convert the virgin hair surface from a hydrophobic, entity with little surface charge to a more hydrophilic, more polar and more negatively charged surface; see Chap. 6 for additional details. Cystine degradation occurs inside cuticle cells in the cystine rich A-layer and the exocuticle of the cuticle and in cortical cells because tensile results show that cystine degradation occurs in the matrix of the cortex too and likely in the Intermediate Filaments too; however the strongest effects are in the uppermost surface layers [6]. Cystine and tryptophan, methionine, tyrosine, histidine and lysine are also modified by oxidation. With long term or extensive sunlight exposure, peptide bonds are degraded by sunlight forming new cross-links which first occurs in the cuticle layers and ultimately in the cortex.

5.5 Mechanisms for Free Radical Reactions in Human Hair

Kirschenbaum et al. [66] provided evidence from photo-irradiation of human hair under UVA and visible light for the formation of the hydroxyl free radical. Their results showed that bleached and red hair provide a greater yield of hydroxyl

radicals than brown hair. This latter effect is due to the fact that there is more eumelanin in brown than bleached and red hair and it is a more effective radical scavenger than pheomelanin.

Millington [67] in a review on photoyellowing of wool describes the formation of hydroxyl radicals, oxygen radicals, superoxide and hydroperoxides as being the species that drive photoyellowing reactions. Millington described the generation of hydroxyl radicals in several schemes as in the initial photo-chemical excitation of a photo-chemical absorber or radical initiator such as melanin [67–69] pheomelanin or tryptophan [66, 67].

$$\text{Initiator} + \text{hv} \rightarrow \text{Initiator}^{*}\{\text{Initiator}^{*} \text{ denotes excited state}\}$$

The second step is the formation of free radicals from the excited state of the initiator.

$$\text{Initiator}^{*} \rightarrow \text{B}^{\bullet} + \text{C}^{\bullet}$$

The next step involves abstraction of a hydrogen atom from the keratin fiber to form a free radical on the hair or wool keratin.

$$\text{B}^{\bullet} + \text{Keratin-H} \rightarrow \text{Keratin}^{\bullet} + \text{B-H}$$

Propagation then occurs by reaction with oxygen forming a hydroperoxide of the keratin.

$$\text{Keratin}^{\bullet} + \text{O}_2 \rightarrow \text{Keratin-OO}^{\bullet}$$

$$\text{Keratin-OO}^{\bullet} + \text{ Keratin-H } \rightarrow \text{Keratin-OOH} + \text{Keratin}^{\bullet}$$

The Keratin hydroperoxide can react with either a transition metal like Fe or Cu that is either in solution or in the fiber or with light to form a hydroxyl radical and a Keratin hydroxyl radical to continue the chain reaction.

$$\text{Keratin-OOH} + \text{hv} \rightarrow \text{Keratin-O}^{\bullet} + \text{HO}^{\bullet}$$

$$\text{Keratin-OOH} + \text{Metal } \rightarrow \text{Keratin-O}^{\bullet} + \text{HO}^{-} + \text{Metal}^{+1}$$

Another scheme to provide Hydroxyl radicals along with hydrogen peroxide and superoxide was described by Millington [67] in this same review. In this scheme, a chromophore such as melanin or Tryptophan can absorb light and be elevated to an excited state.

$$\text{Chr} + \text{hv } \rightarrow \text{Chr}^{*}$$

The excited chromophore can then react with molecular oxygen to form superoxide anion radical.

$$Chr^{*} + O_2 \rightarrow \ Chr^{+\bullet} + {O_2}^{-\bullet}$$

Dismutation of superoxide then occurs to hydrogen peroxide and molecular oxygen.

$$2{O_2}^{-\bullet} + 2H^{+} \rightarrow \ H_2O_2 + O_2$$

Hydrogen peroxide can then react with either a transition metal (Fenton reaction; primarily ferrous or cuprous ion) or by photolysis to form hydroxyl radicals. In the case of hydrogen peroxide oxidation of hair, H_2O_2 is already present, and if Cu or Fe is present, then the Fenton reaction (below) can occur to produce hydroxyl radicals.

$$H_2O_2 + hv \ \rightarrow 2HO^{\bullet}$$

$$H_2O_2 + \text{Metal} \ \rightarrow HO^{\bullet} + OH^{-} + \text{Metal}^{+1}$$

Millington proposed these schemes to provide hydroxyl radicals, hydroperoxides and oxygen radicals that he felt were important to the yellowing mechanism of wool fiber. Hydrogen peroxide can also be generated during the photo-degradation of Tryptophan which can then generate hydroxyl radicals by either reacting with trace metals or by photolysis. These reactions involving hydrogen peroxide or keratin hydroperoxides, especially with metals such as Cu or Fe, are very relevant to the reaction of alkaline hydrogen peroxide with human hair during bleaching or oxidative dyeing.

Millington discussed different photo-yellowing mechanisms and concluded that the evidence supports that the yellowing of wool fiber is caused by the photo-oxidation of several species and not just the photo-oxidation of tryptophan to N-formyl kynurenine to kynurenine and finally to 3-hydroxy kyneureine that has been shown to occur in wool fiber [70].

Superoxide anion radical has been shown by Bruskov et al. [71] to be generated by heating aqueous buffers containing oxygen and transition metal ion impurities. In this reaction, molecular oxygen is excited to singlet oxygen which is reduced to superoxide by the metal. Millington [67] pointed out that some dyes in the presence of an electron donor can generate superoxide radical and hydrogen peroxide by an electron transfer mechanism. In addition, Misra [72] pointed out that superoxide radicals are formed by autoxidation of a large number of compounds including simple thiols, some iron complexes and reduced flavins and quinones.

These reactions are all fundamental to the reactions that can occur in human hair particularly in those regions of the fiber where metals like Fe and Cu exist or where even low ppm levels of Cu or Fe are in the water supply.

5.5.1 The Formation of Sulfur Type Free Radicals in Keratin Fibers

The events occurring when human hair is exposed to sunlight involve photo-degradation of the disulfide bond. This reaction affects the wet tensile properties. In addition, the surface becomes more hydrophilic. Photo-degradation of the thioester groups occurs at the surface and in the Beta layers of the cuticle CMC. A yellowing reaction occurs that involves tryptophan, cystine and other amino acids in the cuticle, the cortex and other areas involving light or heat. Bleaching of hair pigments occurs in cortical cells (most but not all of pigment granules are inside cortical cells; a few are in between in the cortex CMC [73]), and hair fibers become more sensitive to cuticle fragmentation (involving disulfide bonds inside cuticle cells and the other bonds in the cuticle CMC) and to axial fracturing which involves events occurring in the cortex CMC.

The best description of the mechanism of photo-degradation of the disulfide bond that I could find has been described by Millington and Church [74]. Any mechanism to account for the changes occurring to cystine when keratin fibers are exposed to sunlight must account for an increase in three products, cysteic acid, cysteine S-sulfonate and cysteine (thiol) groups [74]. When keratin fibers are exposed to sunlight, UVB radiation in the range of 280–320 nm is absorbed by tyrosine and tryptophan residues and both of these species are excited to a higher energy level [74].

$$\mathrm{Tyr} + \mathrm{hv}(280-320\,\mathrm{nm}) \rightarrow {}^{1}\mathrm{Tyr}^{*}$$

$$\mathrm{Trp} + \mathrm{hv}\,(280-320\,\mathrm{nm}) \rightarrow {}^{1}\mathrm{Trp}^{*}$$

The energy absorbed by tyrosine is transferred to other groups including tryptophan and cystine.

$${}^{1}\mathrm{Try}^{*} + \mathrm{Trp} \rightarrow {}^{1}\mathrm{Trp}^{*} + \mathrm{Tyr}$$

It has been known for some time that cystine is an effective quenching agent for tyrosine and tryptophan in proteins and the quenching mechanism has been described as an electron transfer process forming this type of radical anion: $\mathrm{RSSR}^{\bullet-}$

Several papers discuss the quenching by cystine disulfide in proteins when tyrosine or tryptophan nearby or adjacent to cystine in a polypeptide chain [75]. It is possible that cystine quenching of tryptophan or tyrosine could be involved in the reaction of alkaline peroxide with human hair. However, the radical anion of cystine residues (above) can also form by one electron transfer involving metal ions. This reaction is highly likely in the oxidation of human hair [76] with hydrogen peroxide. Furthermore, radical anions of disulfides dissociate to form an equilibrium with a thiol anion and a thiyl radical as indicated below.

$$RSSR^{\bullet -} \rightleftharpoons RS^{-} + RS^{\bullet}$$

The thiyl radical can then add oxygen to form an SII oxidized state.

$$RS^{\bullet} + O_2 \rightarrow RSOO^{\bullet}$$

This SII radical can rearrange to form the SVI radical.

$$RSOO^{\bullet} \rightarrow RSO_2^{\bullet}$$

The SVI radical can add oxygen to form the hydropersulfate radical.

$$RSO_2^{\bullet} + O_2 \rightarrow RSO_2\text{-}OO^{\bullet}$$

The hydropersulfate radical can abstract a hydrogen atom to form the hydropersulfate.

$$RSO_2\text{-}OO^{\bullet} + R\text{-}H \rightarrow R^{\bullet} + RSO_2\text{-}OOH$$

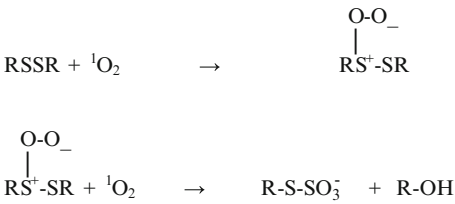
The hydropersulfate can similarly be reduced to form the sulfonate and water.

$$RSO_2\text{-}OOH \rightarrow RSO_3H + H_2O$$

In this reduction reaction, the hydropersulfate can generate hydroxyl and other radicals.

5.5.2 *Proposal for the Photochemical Mechanism for C–S Fission of Disulfides*

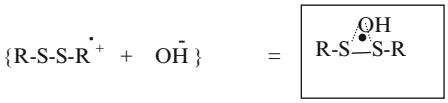
The mechanism for the formation of cysteine S-sulfonate has not been totally resolved. Millington and Church [74] proposed that since the S-sulfonate is formed at higher wavelengths (UVA range and the higher the wavelength of radiation the more cysteine S-sulfonate formed) singlet oxygen is most likely involved as a competing mechanism involving attack on the disulfide to form a zwitterionic species as proposed by Murray and Jindal [77]. Millington and Church [74] suggested this zwitterion could rearrange to produce the S-sulfonate (Bunte salt). However, Millington and Church did not explain exactly how the rearrangement would occur. This species could produce the S-sulfonate with additional oxidation as suggested below. This reaction could involve singlet oxygen or molecular oxygen.



Millington and Church cited a reference by Schmidt [78] showing that singlet oxygen is not produced at low UV wavelengths such as 265 nm but is present after radiation at 350 nm.

5.5.3 *Photochemical Reaction of Disulfide with Hydroxyl Radical in Aqueous Solution*

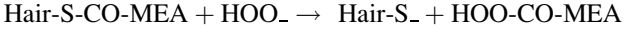
The above oxidation of the disulfide bond induced by photolysis involves the formation of singlet oxygen or the disulfide anion radical generated by various means. Bonifacic et al. [79] studied the primary steps in the reactions of organic disulfides with hydroxyl radicals in aqueous solution and identified the formation of a radical cation adduct as a key intermediate of this reaction:



The primary fate of this adduct radical depends on the pH of the medium. In basic solution, the primary initial products are thiols and R-S-O$^{\bullet}$ (sulfinyl radical) formed most likely by SN2 substitution of RS^{-} by OH^{-}. Ultimately these materials (thiols and sulfinyl radicals) can be oxidized to sulfonate.

5.5.4 *Photochemical Reactions of Thioesters in Hair*

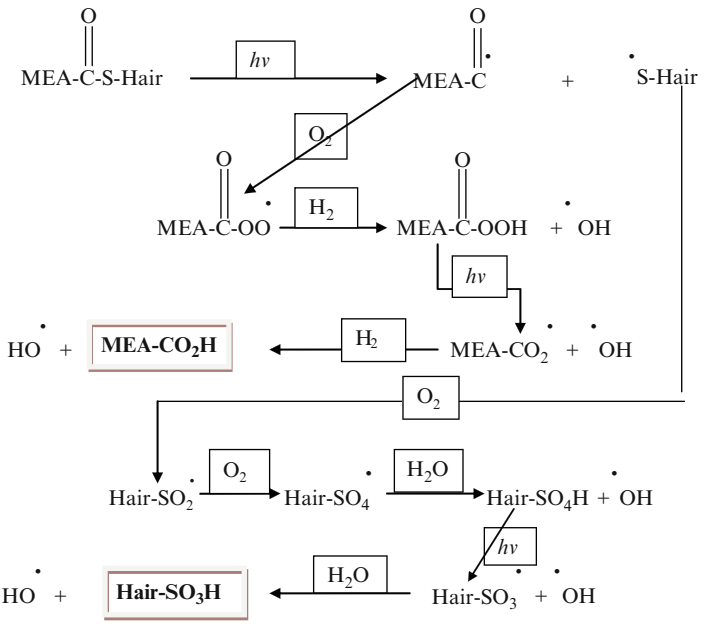
The thioester bond can be cleaved by the hydroperoxide anion or by the hydroxide anion by nucleophilic scission of the thioester link. For nucleophilic attack by the hydroperoxide anion one mole of the peroxy acid of MEA will be created, another source of hydroxyl free radicals.



The thiol group can then be oxidized by oxygen, by hydrogen peroxide or the peroxy acid to Sulfonate. In the case of oxygen the first step is the oxidation to the disulfide. With oxygen, this reaction can be catalyzed by Fe or Cu and the formation of a metallic ion-thiol complex is believed to be responsible for increasing the rate of this oxidation with oxygen [80, 81].

The reaction of sunlight on thioester is very different. A mechanism for this reaction is summarized below. The first step in the mechanism for the oxidation of thioester in sunlight involves the formation of an acyl and thiyl radical by the action of ultraviolet light acting on the thioester group. Takahashi et al. [82] and Chatgilialoglu et al. [83] have shown that the formation of acyl radicals from different acyl groups including thioesters occurs by the action of ultraviolet light. Takahashi [82] confirms by the following quote that this is a well accepted reaction, "it is well accepted that upon irradiation, thioesters undergo homolytic cleavage to form an acyl and a thiyl radical pair with subsequent reaction." The paper by Brown et al. [84] describes several free radicals formed in hexane or di-t-butyl peroxide solvent at room temperature using 308 nm laser flash photolysis on aldehydes or ketones. Among the acyl radicals generated were $CH_3C^{\bullet}{=}O$; $CH_3{-}CH_2{-}C^{\bullet}{=}O$; $(CH_3)_3CC^{\bullet}{=}O$; and $C_6H_5C^{\bullet}{=}O$ and these acyl radicals are analogs to the acyl radical that would be formed from 18-MEA attached to the hair surface. In addition, some of the corresponding acyl peroxyl radicals were formed in the work by Brown et al. by reaction of the acyl radicals with oxygen similar to what is proposed in the mechanism described below.

Proposed Mechanism for the Oxidation of Thioester in Hair by Sunlight:



The above oxidation of thiol may not proceed through the disulfide bond because of "Proximity", that is, if the thiol groups bound to hair proteins are not close enough to another thiol or sulfur group to form a disulfide bond then that reaction cannot occur. Therefore, this oxidation could bypass the disulfide stage and occur via mobile oxidizing species such as molecular oxygen (superoxide, singlet oxygen, hydrogen peroxide or hydroperoxide anion, etc).

Ruetsch et al. [40] state that for both the chemical (alkaline peroxide) and photochemical oxidation of human hair thioester groups on the surface are converted to sulfonate. However, they do not describe mechanistically how this happens. In describing the chemical oxidation they state, "A side reaction of bleaching is the hydrolysis of the thioester linkages". It is true that some hydrolysis could occur. However since the hydroperoxide anion is a stronger nucleophile than hydroxide anion I would expect more cleavage by the hydroperoxide anion and also by free radical degradation. Nevertheless as indicated, I could find nothing in the hair or wool literature describing this mechanism.

5.5.5 *Carbon Based Free Radicals from Tryptophan and Phenylalanine*

Evidence for the free radical decomposition of tryptophan has been presented by Domingues [85]. Tolgyesi [64] suggested that tryptophan, tyrosine and phenylalanine are involved in free radical formation. The hydroxylation of phenylalanine to tyrosine has been observed by Bringans et al. [70] (confirming the presence of hydroxyl radicals in the oxidation of phenylanine). These references implicate several carbon based free radicals in the chemistry of human hair.

5.5.6 *Free Radicals from Allylic and Tertiary Versus Alpha Hydrogens*

Another important reaction involves formation of carbon based free radicals that produce hydroperoxides and thus are chain propagation reactions. This reaction and the subsequent reactions of its products have already been explained as well as the relative stability of different allylic, tertiary and alpha hydrogen atoms in this Chapter in the section entitled, *Long Term Irradiation Produces Fusion Reactions Across Structural Boundaries*. Furthermore, the preference for allylic free radical formation can be found in most organic chemistry texts such as Ege [86] who explains that allylic free radicals will be formed preferentially over even those at tertiary carbon positions because allylic free radicals are more stable.

5.5.7 *Chlorine Oxidation of Human Hair*

Allworden [87] was the first to treat hair with chlorine and bromine water. Allworden noted that bubbles or sacs form at the surface of the fibers during this type of treatment. This oxidizing system diffuses across the epicuticle membrane

and degrades the proteins beneath the membrane producing smaller, water-soluble proteins and polypeptides too large to migrate out of the hair. At the same time it degrades and weakens the epicuticle. As a result, swelling occurs beneath the epicuticle, due to osmotic forces, producing the characteristic Allworden sacs (see Fig. 1.29).

The qualitative observations of the Allworden reaction are produced by relatively large concentrations of chlorine or bromine water. Fair and Gupta [88] were the first to investigate the effect of chlorine water on hair, at the parts-per-million level, in an attempt to assess the effects of chlorine in swimming pools on hair.

In this study, hair effects were measured by following changes in hair fiber friction. In general, the effect of chlorine was to increase the coefficient of fiber friction and to decrease the differential friction effect. Changes in hair friction were observed even at parts-per-million levels of chlorine. Effects increased with the number of treatments and with decreasing pH from 8 to 2.

The actual oxidizing species present in this system depends on pH and is either chlorine or hypochlorous acid (HOCl). Apparently, hypochlorous acid is the more active species on hair, since degradation is greater at lower pH. Although the chemical changes of these interactions were not examined, one would expect thioester and disulfide bond cleavage and peptide bond fission similar to the effects shown for the reaction of chlorine and wool fiber [89]. For a more complete discussion of these effects see the section in Chap. 1 entitled *Epicuticle and Hair Fiber Structure* and in Chap. 2 entitled *Composition and Components of the Epicuticle*.

5.5.8 Peracid Oxidation of Human Hair

Peracetic acid was the first peracid studied extensively in keratin fiber research. This highly reactive species ultimately became the vehicle used in the well-known keratose method by Alexander and Earland. This method is used to isolate keratose fractions from keratin fibers and is described in Chap. 1 of this manuscript.

Large higher molecular weight peracids such as m-diperisophthalic acid have been studied. Such larger peracids tend to focus the oxidative degradation to the outer regions or the periphery of the fibers producing a ring oxidation effect analogous to ring dying, see Fig. 5.13. This figure contains a cross section of a hair fiber (in water) after reaction with m-diperisophthalic acid for nine treatments. Note the extreme swelling at the periphery of the fiber leaving an intact non-swollen or non-reacted fiber at the core. Figure 5.14 represents an SEM of the surface of an untreated control fiber (dry) in this study. Figures 5.15, 5.16 and 5.17 depict the surface of human hair fibers in the dry state after 3, 7 and 20 treatments for 15-min reaction times with m-diperisophthalic acid compared to the control (Fig. 5.14). Note the folds in the scales, indicating dissolution of scale material. These folds increase as the number of treatments increases producing a matrix-type appearance

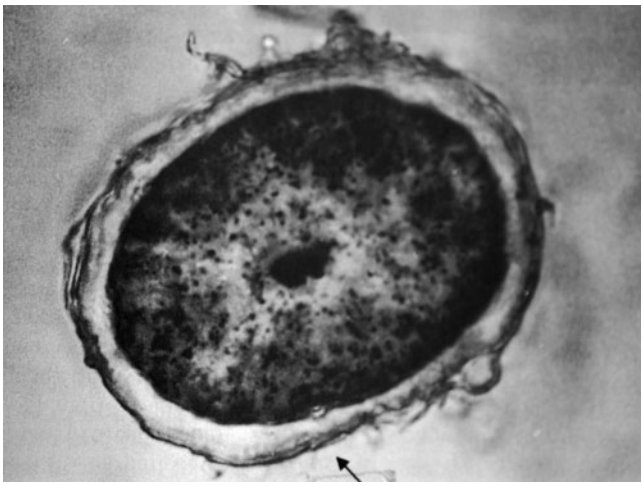


Fig. 5.13 Light micrograph of a cross-section of a hair fiber reacted nine times for 15 min with m-diperisophthalic acid. Note the extensive swelling and cuticle damage in the periphery

Fig. 5.14 SEM of a control fiber prior to treatment with m-diperisophthalic acid. Treatment was on the head of a panelist

after seven treatments. After 20 treatments with this peracid, the complete loss of cuticle scales has occurred, see Fig. 5.17.

Figures 5.18, 5.19 and 5.20 illustrate another perspective of this treatment by viewing the fibers in the wet state in water after different reaction times. Figure 5.18 depicts the effects after three treatments and Fig. 5.19 after six peracid treatments. At this stage, after six treatments, the fibers begin to display an Allworden type reaction in water. After nine treatments, scale material is still present, but the Allworden reaction is only transitory. Apparently, the proteins inside the cell membranes are so degraded that they cause such a large uptake of water that the

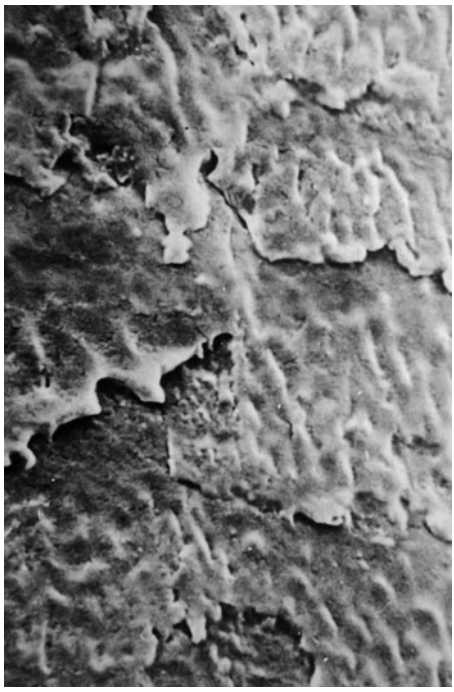


Fig. 5.15 SEM illustrating the hair surface dry after three treatments with m-diperisophthalic acid. Note the axial folds in the scales compared to the control in Fig. 5.14. These folds are created by the loss of cuticular proteins from oxidation

weakened membranes rupture after long water exposures. This effect is analogous to the effects of the long-term exposure of hair fibers to sunlight followed by treatment with alkaline peroxide, described to this author in a private communication by Sigrid Ruetsch.

The light micrograph of the hair fiber in Fig. 5.21 was obtained from a fiber taken directly from the scalp of an individual in a forensic study. However, the treatment was unknown. John T. Wilson a forensic scientist provided this micrograph to me. From the above micrographs, I conclude that this hair was exposed extensively to sunlight and peroxide bleaching. It is interesting that such cuticle scale degradation can be produced on hair on live heads. The hair fiber of Fig. 5.22 shows what appears to be a classical Allworden reaction; however, this effect was obtained after 5 thirty-minute exposures to alkaline hydrogen peroxide that bleached the hair from dark brown to golden brown followed by a single 15-min treatment with m-diperisophthalic acid.

After multiple treatments with m-diperisophthalic acid when bundles of fibers or tresses are allowed to dry the fibers actually appear glued together. These glued fibers are reminiscent of the combined photochemical plus peroxide bleach treatment of Fig. 5.11. Examination of hair fibers treated 12 times with this peracid and dried provided evidence that the fibers are actually glued together (Fig. 5.23). Apparently the proteins of the cuticle are sufficiently solubilized so that some of the proteinaceous glue-like matter migrated out of the scales leaving a gelatin-like

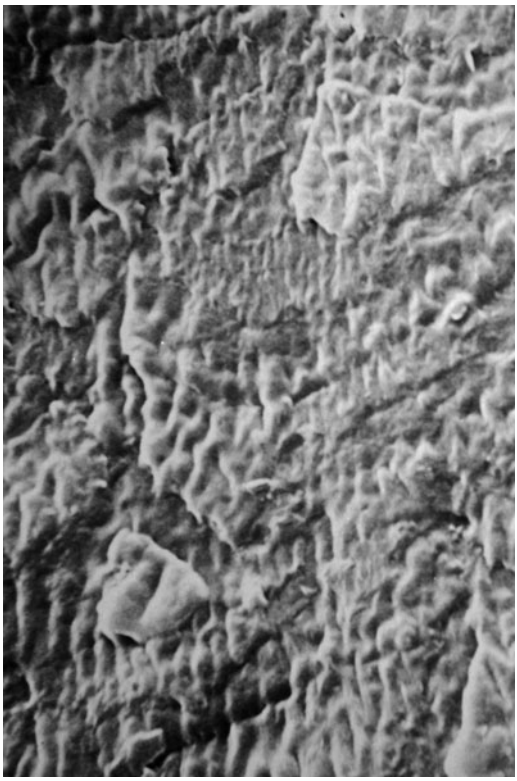


Fig. 5.16 SEM of the hair surface after seven treatments with m-diperisophthalic acid. Note the greater number of folds in the scales compared to Fig. 5.15

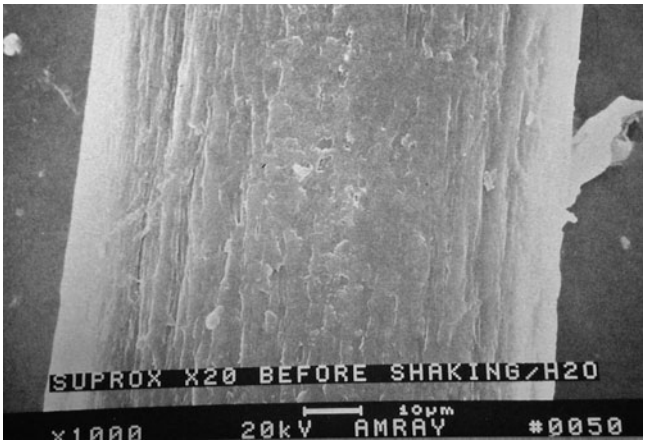


Fig. 5.17 SEM of the hair surface after 20 treatments with m-diperisophthalic acid. Note the complete absence of cuticle scales (Reprinted with permission of the Journal of the Society of Cosmetic Chemists)

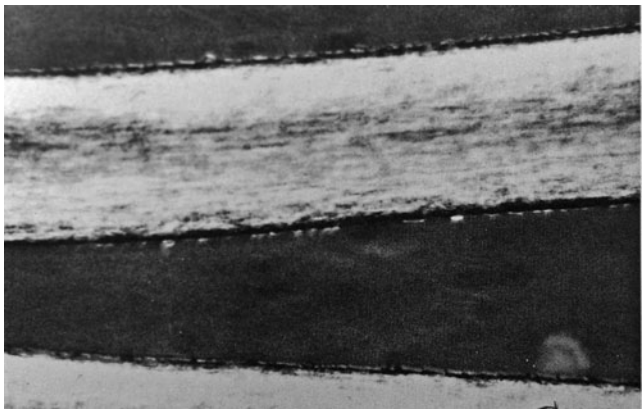


Fig. 5.18 Light micrograph (optical section) illustrating the hair surface in water after three treatments with m-diperisophthalic acid. Note the swelling in the cuticle layers

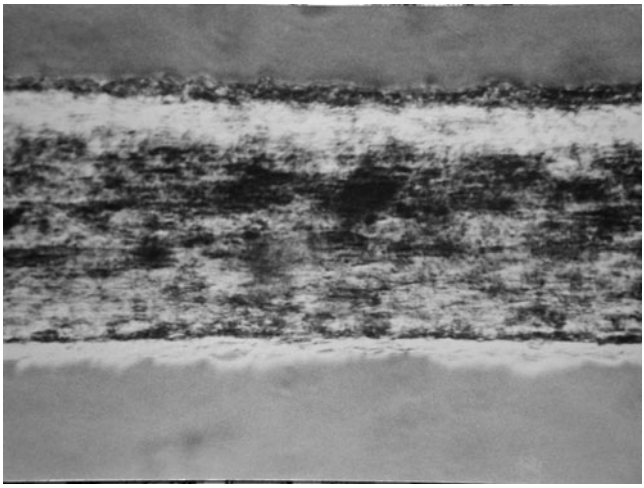


Fig. 5.19 Light micrograph (optical section) illustrating the hair surface in water after six treatments with m-diperisophthalic acid. Note the extensive swelling of the cuticle scales

deposit on drying that actually glued the fibers together. The cuticle scales from fibers of this treatment, Fig. 5.23, appear to be gone over most of the fiber surface, but are actually covered by the proteinaceous deposit. The scales appear only where "glue" has been separated from the underlying scales. After 20 treatments with m-diperisophthalic acid, the scales are totally removed. Fracturing of hair fibers after this peracid treatment has not been examined, but would likely reveal some interesting new findings.

Fig. 5.20 Light micrograph (optical section) of the hair surface in water after nine treatments with m-diperisophthalic acid. Note the extensive swelling and lifting of cuticle scales

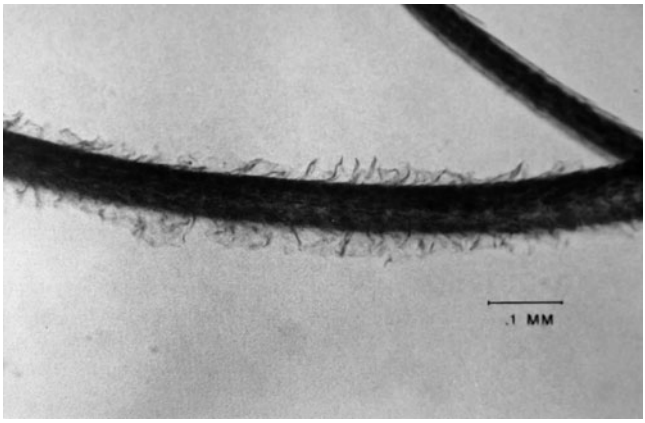


Fig. 5.21 Light micrograph of a damaged hair fiber taken from the head of a forensic study. Treatment unknown, but probably ultraviolet exposed and chemically bleached (Light micrograph kindly provided by John T. Wilson)

5.6 Hair Pigment Structure and Chemical Oxidation

5.6.1 Hair Pigment Production and Pigment in Different Hair Types

The principal pigments of human hair are the brown-black melanins (eumelanins) and the less prevalent red pigments, the pheomelanins. These latter pigments at one time were called trichosiderins. The genes involved in the formation of the

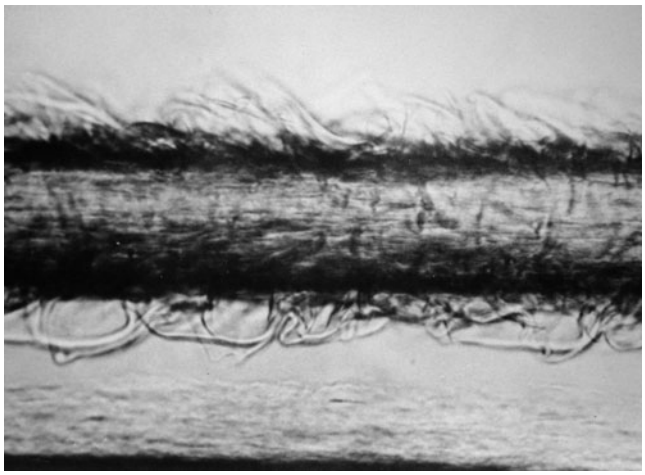


Fig. 5.22 Hair fiber bleached five times for 30 min with alkaline peroxide and then once with m-diperisophthalic acid. Note the large "Allworden" sacs at the surface

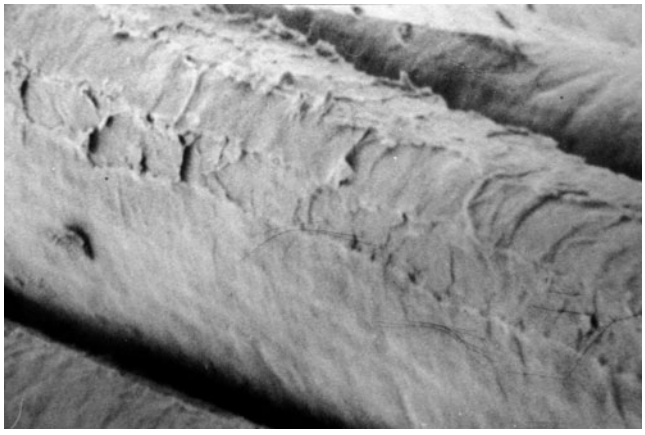


Fig. 5.23 Hair fibers from a tress treated nine times with m-diperisophthalic acid and dried. Note the "apparent" absence of scales on part of the fibers and the presence of scales where the fibers have been pulled apart. After treatment, to the naked eye, the fibers appeared to be glued together until broken apart

melanosomes and different hair colors are summarized in Chap. 3 in the section entitled, *Hair Pigmentation and Genetics*. For the discussion, in this Chapter the brown-black pigments of hair will be referred to as melanins and the yellow–red pigments will be referred to as pheomelanins.

Birbeck and Mercer [90] determined that the pigments in scalp hair reside within the cortex and medulla as ovoid or spherical granules. Barnicot et al. [91] concluded that the pigment granules generally range in size from about 0.4–1.0 μm along their major axis; see Figs. 5.24 and 5.25. These SEMs show some partially dissolved

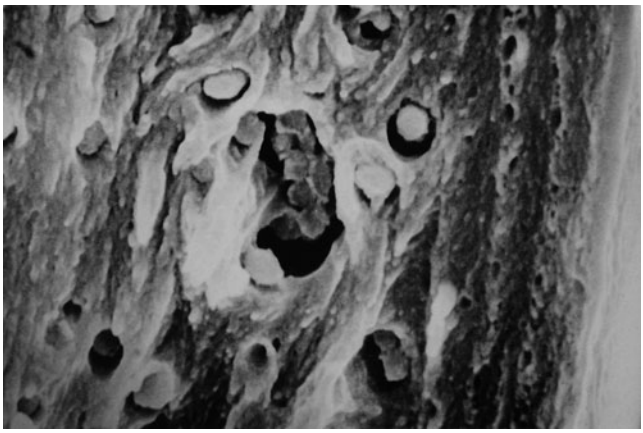


Fig. 5.24 Hair fibers exposed to ultraviolet radiation and then fractured exposing melanin granules (SEM kindly provided by Sigrid Ruetsch)

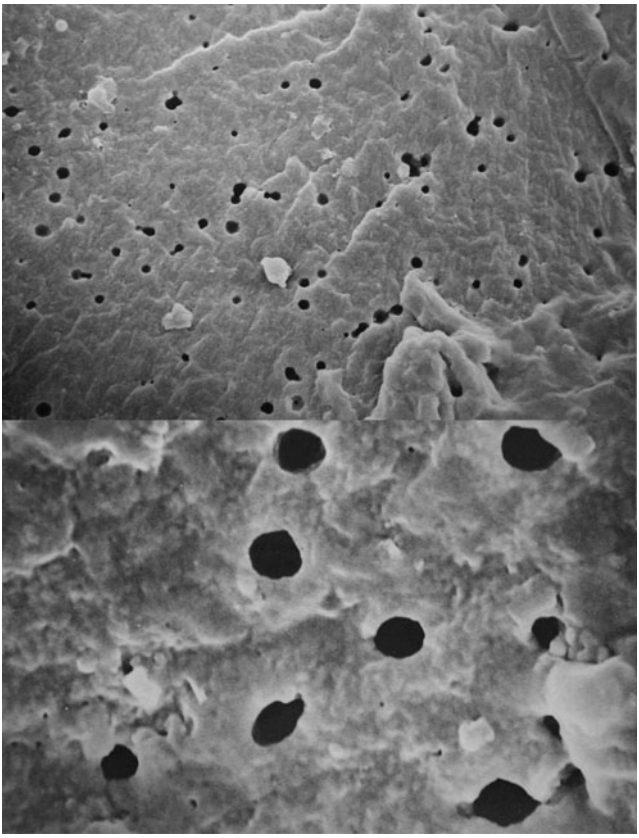


Fig. 5.25 Hair fibers exposed to ultraviolet radiation followed by bleaching with alkaline peroxide and then fractured. Note the holes or vacancies where melanin granules once were SEM kindly provided by Sigrid Ruetsch

melanin granules and some holes or vacancies where melanin granules have been dissolved from the fiber. Hair pigments are produced by the melanocytes (melanin producing cells) and are packed into the melanosomes which are pigment containing granules. The pigment granules are then transferred into the keratinocytes (hair fiber cells). Tobin and Paus [92] suggested that with age there is a deficiency in the melanosome transfer process. A relatively small number of melanocytes are necessary to produce an intensely pigmented hair fiber of 1 m or longer. These melanocytes function in 7–15 hair cycles to produce pigmented hairs for up to four decades or longer [92]. Tobin and Paus also suggested that each melanocyte has a "melanogenesis clock" or each melanocyte can produce a limited amount of melanin which determines a melanocyte lifetime. They concluded that epidermal pigmentation changes are more subtle than those in the graying of hair because the melanocytes in the hair bulb age faster due to the highly intense production of melanin required by hair cycles. Furthermore, the hair graying effect results from a decrease and the eventual termination of the activity of the enzyme tyrosinase in the lower hair bulb. This enzyme is involved in the reaction called Raper's scheme described in the next section in this Chapter.

Figure 5.24 shows pigment granules as they appear inside the fiber. This micrograph was obtained after fracturing photo-oxidized hair. Figure 5.25 also shows ovoid cavities where pigment granules have been dissolved and removed by photo-oxidation and subsequent treatment with alkaline peroxide. Hair pigments are found in the cortex and the medulla and not normally found in the cuticle of scalp hair. Most but not all of the pigment granules are inside cortical cells; some are in between these cells in the cortex–cortex CMC [73]. Menkart et al. [93] concluded that pigment granules generally comprise less than 3% of the total fiber mass, as estimated by the residue weight after acid hydrolysis.

Schwan-Jonczyk [94] suggested that the size of melanin granules, in addition to the total melanin content and type of melanin (eumelanin vs. pheomelanin) determine hair color. For example, she cites that Black African hair contains large eumelanin granules about 0.8 μm along their major axis, while Japanese hair has smaller eumelanin granules about 0.5 μm and blonde European hair contains even smaller primarily pheomelanin granules about 0.3 μm. Schwan-Jonczyk suggested that as a general rule, black hair contains primarily large eumelanin granules, medium to light brown hair contains both eumelanin and pheomelanin granules and blonde hair contains primarily pheomelanin granules that are smaller.

These observations by Schwan-Jonczyk are consistent with those of Swift [95] who several years ago in his Ph.D. thesis reported, via measurements with the electron microscope, that melanin granules from hair of black Africans is larger than those from Caucasian hair. Bernicot and Birbeck [96] determined that the pigment granules from dark European hair are on average larger than those of blonde and red hair which is consistent with Schwan-Jonczyk's conclusions. Fitzpatrick et al. [97] confirmed that the pigment granules of hair of African descendants tend to be larger than those of dark European hair.

The pigment in hair is produced by melanocytes that are associated with each individual hair fiber. Thus, there is no transfer of pigment or melanosomes from one

hair fiber to another during biosynthesis. This fact accounts for hairs of very different pigmentation (colors) growing adjacent to each other. The melanocytes in the skin of Blacks appear similar to those of Caucasians. However, Barnicot and Birbeck [96] state that the pigment granules in the skin of Blacks are larger and more numerous than in the skin of Caucasians, similar to the pigment granules in the hair of Blacks and Caucasians.

This heavy pigmentation in African type hair is very useful in two distinctly different situations. First of all the pigments in hair protect it from many photochemical [98] and thermal reactions such as in straightening of hair with hot irons or presses. These protective actions become more important to Blacks as they age and the graying process begins. Because this protection decreases as the pigments are reduced in the hair. Secondly, hair pigments reduce the amount of light scattered from the hair. Therefore, these pigments help to improve hair luster as shown by Keis et al. [99]. Keis et al. determined that single hairs of African Americans are among the shiniest of hairs [99]. It is only because of the high coiling and poor alignment that an array of African type hair appears dull. Therefore, curly to highly coiled hair of Blacks that is often thought of as not being shiny would be even less shiny if it contained less pigment.

Fine hair tends to be lighter in color than coarse hair. The extreme case supporting this statement is that vellus hair, the finest of all hairs does not contain pigment, whereas most permanent hairs that is the coarsest of hairs generally contain pigment. Caucasian hair on average is finer than Asian or African hair and it also tends to be lighter in color.

There are likely exceptions to this conclusion that fine hair tends to be lighter in color than coarse hair. Exceptions are likely because hair color is determined by several variables including the type of melanin pigment present, the size of the pigment granules and the density (frequency) of the pigment granules that are dispersed throughout the cortex of human scalp hair fibers. Nevertheless, there are several other references (below) supporting this conclusion.

Pecoraro et al. [100] examined hair from 26 infants within 76 h of birth considering hairs from 13 males and 13 females and found that the mean coarseness of dark hairs from dark complexioned newborns was 37 μm while the average diameter for light colored hairs from light complexioned newborns was 22 μm.

Trotter and Dawson [101, 102] examined hair from 310 children and adult Caucasians (French Canadians) and found that more coarse hair tends to be darker than finer hair [101, 102], see Table 5.7. In addition, Bogaty [103] has shown in his review of the anthropological literature that Caucasian children's hair is on average finer, rounder, less frequently medullated and lighter in color than adult's hair.

One possible exception to the above conclusion is gray hair. The graying process in terms of comparisons of gray to white and dark hair needs additional study, however, we do know there is less pigment in gray hair than in dark hair. Most likely the pigment granules of gray hair are also smaller in size, both actions a result of changes in the melanization process with ageing described above. Hollfelder et al. [104] have provided evidence from five Caucasians that gray hairs on the same

Table 5.7 Caucasian children's hair tends to be finer and lighter than adult's hair[a] [101]

Ages	N	Diameter (μ)	Brown–black	Blond–dark blond	Light blond
0–4	46	58	35	50	15
5–9	36	66	75	22	3
10–14	45	69	96	4	0
15–19	56	74	98	2	0
20–29	52	73	98	2	0
30+	75	70	97	3	0
	310				

[a]Data from Anthropological study of French Canadian hair by Trotter and Dawson [102]

person are coarser and wavier than highly pigmented hairs. This observation by Hollfelder et al. is consistent with observations by Yin et al. [105] that fine Caucasian hair is straighter than coarse Caucasian hair.

Van Neste [106] examined approximately 60 hairs from each of three different scalp sites (left and right top of head and occipital) from 24 women. Twelve of these women were menopausal with an average age of 59.6 and 12 were premenopausal and younger but the average age was not given. A total of 3,343 hairs were examined after classification as pigmented (P) and non-pigmented (W). The average diameter of W hairs exceeded the P hairs by 10.27 μm, $p = 0.0001$. The medulla of W hairs was more developed than in the P hairs, $p = 0.0001$ and the growth rate of the W hairs was about 10% faster than the P hairs. This study is in agreement with the one by Hollfelder et al. suggesting that gray-white hairs are coarser than pigmented hairs.

However, Gao and Bedell [107] studying gray hair and dark hairs from four persons plus one sample of pooled gray hair, measured cross-sectional parameters with a laser-scanning micrometer and found no significant differences in the maximum center diameter, center ellipticity and cross-sectional areas; however the center minimum diameter of the black fibers were slightly larger than for those of gray hairs. At this time, there is more evidence favoring that gray hairs are coarser than pigmented hairs; however, the evidence is not overwhelming.

Coarser gray hairs would reinforce the thought proposed by several that the medulla is involved in graying, because the medulla at one time appeared to be involved in the genetic abnormality of pili annulati or ringed hair. This abnormality appears as bands or rings of silver or gray and dark regions along the fiber axis. But, ringed hair has been shown to contain bands with and without holes in the cortex along the axis, and these bands correspond to the gray and dark bands. For a more complete description of ringed hair, see Chap. 1.

Nagase et al. [108] demonstrated that hair with a porous medulla gives a whitish appearance with lower luster. These scientists actually measured a decrease in color from hair with a porous medulla. This effect is attributed to an increase in the scattering of light by the medullary pores, part of which is due to a change in refractive index by the hair to air interfaces at medullary spaces. Therefore, gray hair can be made whiter by a porous medulla which adds to the primary effect of graying produced by less pigment.

As indicated, hair pigments function to provide photochemical protection to hair proteins and lipid structures especially at lower wavelengths where both the pigments and hair proteins absorb light (primarily between 254 and 350 nm). Hair pigments absorb light and dissipate the energy as heat. Thus, the pigments are slowly degraded or bleached and in that process they inhibit or minimize degradation to the structural proteins and lipids of hair, inhibiting hair damage which can be detected in the tensile properties [107].

Methods for pigment granule isolation usually involve dissolving the hair from the granules [13, 91, 109–115]. Laxer [112] described a non-hydrolytic method involving reflux for 24 h in a phenol hydrate-thioglycolic acid mixture. The general composition of melanin granules consists of pigment, protein, and minerals. Flesch [13] reported a similar general composition for the pheomelanin-containing granules. Schmidli et al. [113, 114], after acid or alkaline hydrolysis of hair, isolated melanin combined with protein and suggested that melanin exists in combination with protein in the granules, sometimes referred to as melanoprotein.

Since the pigment granules of human scalp hair are located primarily in the cortical cells and the medulla, it is reasonable to assume that pigment degradation by chemical means is a diffusion-controlled process. However, evidence supporting this contention is not available at this time. In fact, determining the rate-controlling step in this process is a large-order task, since it is difficult to quantitatively follow the loss of pigment in hair. Furthermore, two important side reactions consume oxidizing agent: the previously described oxidation of amino acid residues [5] and, in addition, dibasic amino acid residues of hair associate with many oxidizing agents, including hydrogen peroxide and persulfate [115, 116].

5.6.2 Eumelanins and Pheomelanins: Their Biosynthesis and Proposed Structures

As indicated, melanins are synthesized in melanocytes (melanin producing cells) in structures called melanosomes; eumelanin from the amino acid tyrosine and/or phenylalanine and pheomelanin from tyrosine and cysteine.

Raposo et al. [117] described the development of melanosomes in four stages. Five stages are presented here. In early development, melanosomes appear as round amorphous vesicles. Yasumoto and Hearing [118] demonstrated that the gp100 protein (Pmel17) generates structural changes in melanosomes producing fibrillar elliptical melanosomes from the amorphous vesicles. After these structural changes other proteins including melanogenic enzymes, pH regulators and transport proteins are targeted to the melanosomes which begin synthesis of the melanin pigments. When the melanosomes are filled with pigments the melanosome granules are transferred to keratinocytes the cells that form the shaft of hair fibers.

Donatien and Orlow [119] suggested that melanin is deposited in melanosomes on a protein matrix inside the melanosomes. Donatien and Orlow [119] identified the si locus and membrane-bound p locus proteins as melanosomal matrix proteins.

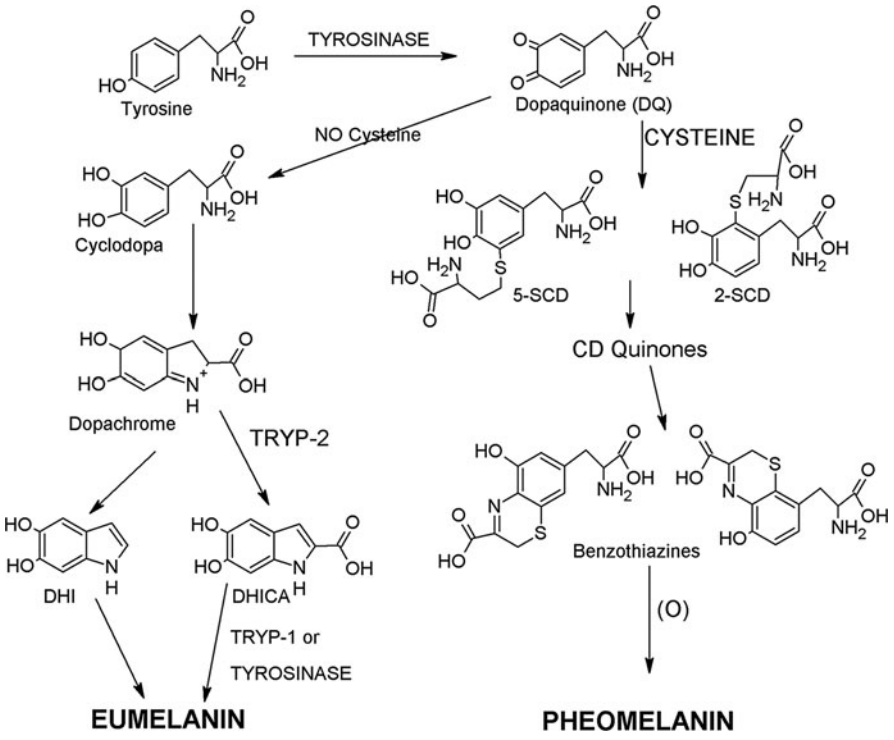


Fig. 5.26 Biosynthetic pathway for the formation of eumelanin, pheomelanin and mixed melanins proposed by Ito and Wakamatsu [131]

Melanin containing melanosomes ultimately become melanin granules after being transferred into keratinocytes.

The intensity or depth of hair color is related to both the size of the melanin granules and the total melanin content or the melanin granule density. In addition, the proportion of eumelanin to pheomelanin is also important, but not the only factor in determining the shade of hair color. Orlow et al. [120] prepared dihydroxyindole-2-carboxylic acid (DHICA) (see Fig. 5.26) enzymatically and via chemical synthesis. Orlow et al. then polymerized DHICA to form brown melanin type polymers that were soluble above pH 5. They also formed black, insoluble melanin precipitates from dihydroxyindole (DHI), dopa or dopachrome (see Fig. 5.26).

When DHICA was in molar excess, mixtures of these two monomers (DHI and DHICA) under the same reaction conditions formed brown melanins. However, black melanins were formed when DHI was in excess. A similar color effect likely exists for natural melanins in human hair. It is also possible that an analogous situation occurs for pheomelanin for intermediates in this process (see Fig. 5.26) causing shifts from yellow to red or perhaps even from brown to red to yellow. At this stage 5-cysteinylDOPA is one of the preferred intermediates in the pheomelanin pathway.

Schwan-Jonczyk [94] suggested that Black-African hair contains ovoid or spherical eumelanin granules about 0.8 μm along their major axis existing as single granules or aggregates. Asian hair contains single melanin granules about 0.5 μm while dark blond European hair contains agglomerates of pheomelanin granules about 0.3 μm along their major axis [94]. As a general rule the darker the hair the higher proportion of eumelanin to pheomelanin in the granules and dark hair generally contains very little pheomelanin.

From cross-sections of African hair vs. dark-brown Caucasian hair the melanin granule density clearly appears higher in African hair. Publications by Kita et al. [121, 122] on melanin granule size and density in East Asian hair reported a higher melanin density in the outer cortex vs. the inner cortex which is typical of Caucasian and African hair too. These scientists found no difference in melanin granule size and density in infant hair compared to 20–30 year olds. However, the minor axis of the granules was significantly smaller at age 60–70 than for the other age groups. The density of the melanin granules was also lower at the advanced age than for the other two age groups [121, 122].

5.6.3 Degradation Products of Melanins

Several years ago, R.A. Nicolaus, G. Prota and others [123–125] isolated a few pyrrole carboxylic acids and indole derivatives from degradation studies of melanins. Two of the pyrrole derivatives were pyrrole-2,3-dicarboxylic acid (PDCA) and pyrrole-2,3,5-tricarboxylic acid (PTCA). PDCA has been suggested by Ito [126] and Borges et al. [127] as a marker for 5,6-Dihydroxyindole (DHI) and PTCA a marker for 5,6-dihydroxyindole-2-carboxylic acid two important monomeric units suggested by Ito and Wakamatsu [128] to create the oligomers that comprise the eumelanin polymer in hair and skin (see Fig. 5.27).

Pyrole tricarboxylic acid (PTCA) and pyrole dicarboxylic acid (PDCA) are degradation products of eumelanins formed from oxidation with either permanganate or alkaline peroxide [123–125, 127]. Other degradation products have been isolated from pheomelanins and used for analysis or for proposing structures [129], see Fig. 5.27. Napolitano et al. [129] have shown that AHPs, 3-AT, BTCA and TTCA are degradation products of pheomelanins. The former two from hydroiodic acid hydrolysis and the four from alkaline peroxide oxidation.

Several degradation products of eumelanins and pheomelanins are depicted in Fig. 5.27. Analytical schemes have been described using these degradation products as markers for eumelanin and pheomelanin. Oxidation with acidic permanganate and alkaline peroxide has been used with both eumelanins and pheomelanins. Oxidation of DHICA melanins provides PTCA as a marker and DHI melanins provide PDCA, however, the yields of PDCA are so small that a large multiplying factor must be used to approximate the amount of DHI melanin. This multiplier provides a potentially large error especially in eumelanin plus pheomelanin

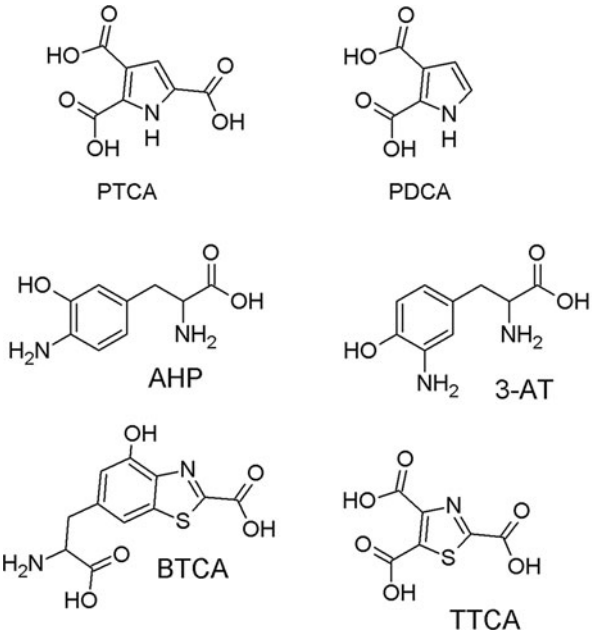


Fig. 5.27 Degradation products of eumelanins and pheomelanins. PTCA and PDCA are produced by either acidic permanganate or alkaline peroxide oxidation of eumelanins. PTCA is considered a marker for DHICA eumelanins and PDCA a marker for DHI eumelanins. AHPs (AHP and 3-AT) are produced by HI hydrolysis of pheomelanins. AHP is considered a marker for pheomelanin, while 3-AT its isomer is considered to interfere in the determination and should be separated from AHP

(smaller multiplying factor) comparisons. In some instances PTCA is used as an indicator of total eumelanin.

Alkaline peroxide oxidation of pheomelanins provides TTCA in low yield; however much higher yields of AHPs are provided by HI hydrolysis of pheomelanins. For the two amino hydroxyl phenylalanines (AHPs) depicted in Fig. 5.27 the 4-amino-3-hydroxy phenylalanine has been called specific AHP by Ito, Wakamatsu and Rees [130]. This term, specific AHP, is used because that isomer is provided in higher yield from pheomelanin and because the other isomer, 3-AT of Fig. 5.27, can be produced by HI hydrolysis of certain proteins which interferes in the AHP analysis for pheomelanin [130].

5.6.4 Biosynthetic Pathway for Mixed Melanogenesis

Several papers have shown that in the formation of most natural melanins, for human hair or skin, mixed melanogenesis occurs rather than exclusively forming eumelanin or pheomelanin [127, 131]. Ito and Wakamatsu [131] in an important paper proposed the biosynthetic pathway for formation of mixed melanins summarized in Fig. 5.26. In this pathway, tyrosine is oxidized by the enzyme tyrosinase to dopaquinone (DQ). This enzymatic reaction occurs faster near neutral than at acidic pH. When cysteine is present above a concentration of about 0.13 μmolar then S-cysteinylDOPAs are formed; however 5-ScysteinylDOPA is the preferred intermediate. 5-ScysteinylDOPA rapidly cyclizes internally to the

corresponding benzothiazine or other intermediates as suggested by Napolitano et al. [132]. These are in turn oxidized to pheomelanin oligomeric units and then to red-yellow pheomelanin polymers.

Chintala et al. [133] proposed via experiments with mice that the SNP Slc7a11 forms a protein that transports either cystine or glutathione (a tripeptide containing cysteine) to the melanosomes. A reducing agent such as βME is necessary to reduce the disulfide bonds of cystine to form cysteine for pheomelanin production. A related process must also occur with cystine or glutamate transport/reduction for pheomelanin formation in human hair. However, this process has not been described prior to this writing.

If cysteine is not present or below the critical concentration of 0.13 μmolar then the eumelanin pathway is followed and cyclodopa is formed from dopaquinone. Cyclodopa then cyclizes internally to dopachrome; pH is also important to this reaction which occurs faster near neutral than at acid pH. In the next step, the enzyme TRYP-2 prevents the decarboxylation of dopachrome allowing the formation of DHICA. If TRYP-2 is absent decarboxylation occurs forming DHI. Both DHI and DHICA are capable of polymerizing to form eumelanin type polymers. However, when the DHICA concentration is above that of DHI, brown melanins are formed. But, when the DHI level is higher, black melanins are formed.

Ito and Wakamatsu [131] concluded that when tyrosine concentration is high and cysteine is low and the pH is near neutral, the eumelanin pathway is preferred. Therefore, higher ratios of eumelanin/pheomelanin are formed. However, when tyrosine concentration is low and cysteine concentration is high and the pH is acidic the pheomelanin pathway is preferred. In that case lower ratios of eumelanin/pheomelanin are formed.

5.6.5 Casing Model for Mixed Melanogenesis

Ito and Wakamatsu [131] proposed a casing model for mixed melanogenesis which appears to be the predominant pathway for formation of the pigments in human hair fibers and in skin. This model is becoming more widely accepted because most natural pigments of hair and skin contain both eumelanin and pheomelanin [130]. For example, Thody et al. [134] found eumelanin and pheomelanin in samples of epidermis from 13 Caucasian subjects with different types of skin. In addition they found that the relative proportions of eumelanin to pheomelanin in the hair of these same subjects correlated with the relative proportions in skin.

In the casing model, DQ is first formed by oxidation of tyrosine by tyrosinase. Then cysteine reacts with DQ to form cysteinylDOPAs which cyclize and oxidize to form pheomelanin molecules. These reactions occur in the membrane of melanosomes. Pheomelanin molecules are apparently released to the interior of the melanosome where they aggregate or cluster to form a core of pheomelanin. A switch then occurs to begin the production of eumelanin as described in the biosynthetic scheme summarized in Fig. 5.26. Eumelanin polymers are then

released to the interior of the melanosome where they deposit on top of the core of pheomelanin. Thus, the final hair color, its intensity and shade are influenced by the thickness and the uniformity of the eumelanin coating as well as by the size of the core of the pheomelanin. These factors are probably more relevant to the shade of the final hair color than the ratio of eumelanin to pheomelanin.

5.6.6 pH and Melanogenesis

Fuller et al. [135] examined melanocytes from both Blacks and Caucasians. The number of melanocytes and the tyrosinase levels were found to be virtually the same. However, the activity of tyrosinase was nearly tenfold higher in the melanocytes of Blacks. Fuller et al. [135] treated the Caucasian melanocytes with ammonium chloride and with the ionophores nigericin and monensin. These ingredients increased the pH and rapidly increased tyrosinase activity. However, when Smith et al. [136] added sodium hydrogen exchangers (NHEs), which add protons, the activity decreased in Black melanocytes. But, these same NHEs had virtually no effect on the activity of Caucasian melanocytes.

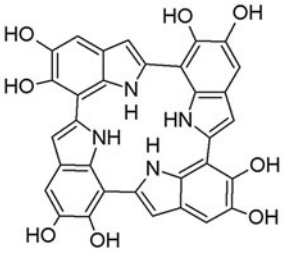
Fuller et al. [135] also found that treatment of Caucasian melanocytes with the weak base acridine orange (a fluorescent staining agent) stains Caucasian melanosomes but not Black melanosomes. This staining reaction suggests that Caucasian melanosomes are acidic and those from Blacks are neutral. Fuller pointed out that it is well known that tyrosinase acitivity is low in acid and higher at neutral pH. Therefore, pH is important to the rate of reactivity of tyrosinase. And higher pH near neutral, produces more eumelanin in melanocytes in the skin of Blacks vs. Caucasians.

Ancans and Tobin et al. [137] examined several different skin types and determined that melanosomal pH determines the rate of melanogenesis, the ratio of eumelanin to pheomelanin and the maturation and transfer of melanosomes to keratinocytes. These scientists also suggested that the P protein is involved in providing the effective pH for these effects. Cheli et al. [138] more recently confirmed the critical role of melanosomal pH in pigmentation and identified cyclic-adenosine monophosphate (c-AMP) and the α-melanocyte stimulating hormone (α-MSH) as important factors for pH control.

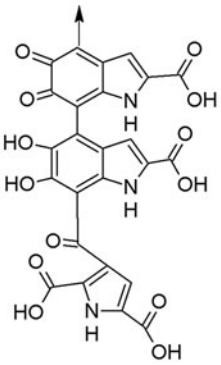
5.6.7 Proposed Structures for Eumelanin and Pheomelanin

5.6.7.1 Proposed Structures for Eumelanin

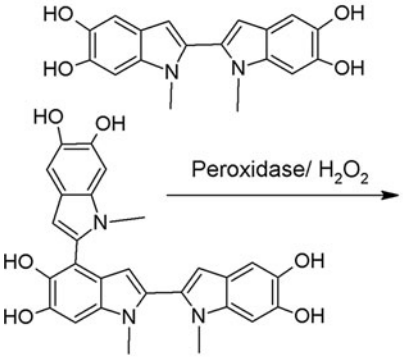
The exact structures for eumelanin or pheomelanin are not known. More than 50 years ago, Mason [139] proposed that melanin consisted of a homopolymer formed from dihydroxyindole. Nicolaus [140] then proposed that melanin is a complex random polymer formed from several intermediates of the Raper scheme,

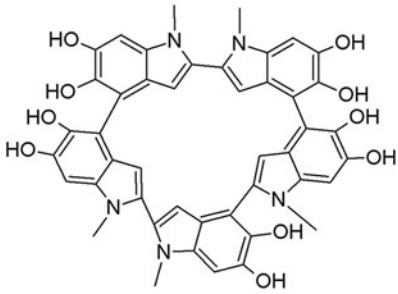


Proposed structure for tetramer of Eumelanin of DHI by Kaxiras et al



Partial structure for Eumelanin proposed by Ito & Wakamatsu. Carboxyls are attached to H or COOH groups and the arrow indicates site for attachment to other units.





Cyclic DHI type Macrocycle isolated by Arzillo et al (2010)

Fig. 5.28 Suggested partial structures for Eumelanin by Kaxiras et al. [143] and by Ito and Wakamatsu [131]. The cyclic structure shown in the *bottom right hand corner* is a structure isolated by Arzillo et al. [144] formed from the dimer and trimer of the dihydroxyindoles shown on the *left* from reaction with peroxidase/hydrogen peroxide under biomimetic conditions

which is essentially the eumelanin pathway described in Fig. 5.26. The Nicolaus proposal is clearly closer to our current point-of-view.

More recently, Napolitano et al. [141] provided evidence that the oligomeric units of synthetic DHICA eumelanins are of low molecular weights (in the range of 500–1500 Daltons) similar to the units suggested by Ito and Wakamatsu [131] in Fig. 5.28. Estimates of the molecular weights of the polymers are higher but these estimates are in question because of the poor solubility and irreversible binding to the chromatographic columns used in the molecular weight analysis.

Ito and Simon [142] described the current view in 2004 of the structure of eumelanins in a concise letter to the editor. Ito provided additional details in

these papers [126, 128, 131, 142] with representative structures for oligomeric units for both eumelanin and pheomelanin [131]. Two suggested representative structures for the oligomeric units of eumelanins are depicted in Fig. 5.28. The structure suggested by Ito and Wakamatsu is based primarily on the degradation products formed from the oxidation of eumelanin and its chemical properties. Actually this structure with a methylene group in place of the carbonyl joining the rings was proposed a few years earlier by Napolitano.

A theoretical structural model for Eumelanin containing only DHI has been suggested by Kaxiras et al. [143] (see Fig. 5.28) and is an interesting one in that it addresses many of the physical and chemical requirements of eumelanin. This structure would theoretically be formed from DHI or its hydroquinone and/or tautomers. These tautomers contain 4 or 5 DHI units to form the basic oligomer which is a porphyrin type ring structure. This type of structure is capable of capturing and releasing a variety of metal ions, an important property of eumelanin pigments. Smaller or larger ring formations are unstable.

Kaxiras et al. [143] proposed that the more stable ring systems which are these tetramer and/or pentamer oligomers would stack in "planar graphite-like arrangements" to form the polymeric structure. This model is consistent with X-ray scattering data of melanin structures. The calculated absorption spectrum for this model suggests it is dark black and thus consistent with DHI-rich eumelanin. However, introducing DHICA and other monomers into this type of model has not been addressed at the time of this writing.

In 2010, Arzillo and Napolitano et al. [144] isolated the macrocyclic structure formed from the methylated dihydroxyindole depicted in Fig. 5.28. This structure was formed by reaction with peroxidase and hydrogen peroxide under biomimetic conditions and provides evidence that structures analogous to the one proposed by Kaxiras et al. [143] can be formed by polymerization of dihydroxyindoles.

5.6.7.2 Proposed Structures for Pheomelanins

A general chemical structure for natural pheomelanins recently proposed by Ito and Wakamatsu [131] is depicted in Fig. 5.29. This structure consists of benzothiazine monomeric units that are combined. This structure is consistent with degradation products and the biosynthetic scheme summarized in Fig. 5.26. However, Napolitano et al. [132] recently monitored the oxidative formation of pheomelanin type products from 5-cysteinylDOPA by liquid chromatography/UV and mass spectrometry and suggested that such structures need reassessment concluding that species such as those summarized in Fig. 5.30, based on absorption properties and reduction behavior, are likely involved in the formation of pheomelanin. Napolitano et al. [132] suggested that "beyond the involvement of 3-oxo-3,4-dihydrobenzothiazine and benzothiazole units it is not possible to go" at this time.

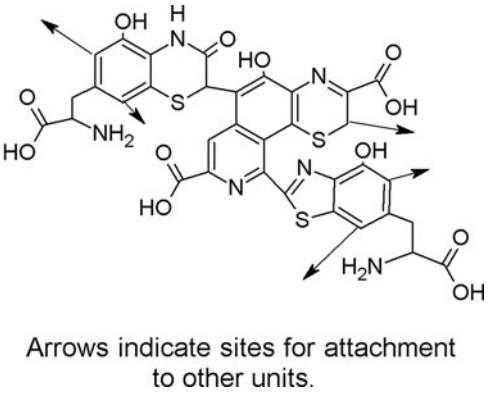


Fig. 5.29 Structure proposed for pheomelanins by Ito and Wakamatsu [131]

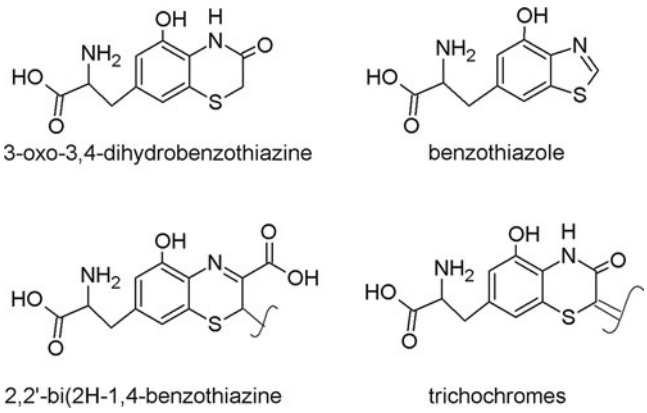


Fig. 5.30 Units suggested for pheomelanins by Napolitano et al. [132]

5.6.8 Degradation Products of Hair Pigments and Different Hair Colors

Use of eumelanin and pheomelanin degradation products (in the section entitled, *Degradation Products of Melanins*) for analysis of human hair of different colors has been provided in several papers. Borges et al. [127] collected and analyzed human hair from 44 subjects: 3 African Americans with black hair, 1 Amerindian with black hair, 6 Asians with black hair, 6 Caucasians with black hair, 2 Hispanics with black hair, 12 people with brown hair, 8 people with blonde hair and 6 people with red hair. Borges et al. determined multiplication factors that they used to approximate the relative amounts of eumelanin and pheomelanin in these hair samples. The data of Table 5.8 shows that black hair contains more total eumelanin than other hair types and red hair has the most pheomelanin or the most CystDOPA (see the biosynthetic scheme of Fig. 5.26 for CystDOPA). Differences of total melanin as

Table 5.8 Analysis of eumelanins in human hair by Borges et al. [127]

Hair color/hair type	μg/eumelanin/mg hair			μg pheomelanin type/mg hair		
	DHI	DHICA	Total eumelanin	2-CystDOPA[a]	5-CystDOPA[b]	Total pheomelanin
Black (African Am.)	8.5	6.0	14.5			
Black (Amerindian)	9.5	5	14.5			
Black (Asian)	7.5	5	12.5			
Black (Caucasian)	4	3	7[c,d]			
Black (Hispanic)	6	4	10			
Brown hair	2	2	4	75	15	90[e,f]
Blonde hair	1.5	1	2.5	75	25	100[e,f,g]
Red hair	1.5	0.5	2.0	650	300	950[e,g]
Black hair				85	15	100[f]

[a]3-AT was used as a marker for 2-CystDOPA (in spite of possible interference [20]) and for these types of distinctions seems to be OK
[b]4-amino-3-hydroxyphenylalanine (AHP) was used as a marker for 5-CystDOPA
[c]Indicates significant difference from African Am. Black hair at $p < 0.01$ level for eumelanin
[d]Indicates significant difference from Asian Black hair for Total eumelanin and DHI only
[e]Indicates significant difference from all Black hair types for eumelanin at $p < 0.0001$ level
[f]Significantly different for pheomelanin for all four hair types analyzed at $p < 0.01$ level
[g]Indicates significant difference from Brown hair at $p < 0.05$ level

large as a factor of 2 were found in the different black hair samples. Borges et al. also found both eumelanin and pheomelanin in all hair samples. However, only low levels of pheomelanin were found in black hair samples.

Some of the conclusions of Borges et al. are summarized below:

- Average black human hair contains about 1% pheomelanin and 99% eumelanin
- Brown and blonde hair contains about 5% pheomelanin and 95% eumelanin and differs primarily in the amount of total melanin present.
- Red hair contains about one third pheomelanin and two third eumelanin. No attempts were made to differentiate between different shades of red hair in this work.

With regard to hair color, Rees [145] suggested that black hair has a high ratio of eumelanin to pheomelanin, whereas red hair has a low ratio of eumelanin to pheomelanin, and blonde hair contains little of either eumelanin or pheomelanin. The data of Borges et al. [127] in Table 5.8 are consistent with these suggestions. The data by Borges et al. suggest that brown hair has slightly higher amounts of eumelanin than blonde hair and nearly equal amounts of DHI and DHICA whereas black hair has more eumelanin and a higher ratio of DHI to DHICA than brown hair.

Napolitano et al. [129] examined 16 different colors of human hair for three pheomelanin markers AHPs, TTCA, BTCA and one eumelanin marker PTCA. Among these 16 different hair colors were Black, Dark Brown, Brown, Blonde, Light Blonde and Albino and 10 different colors of red hair. She also provided the

yield of each marker in ng per mg of hair, but did not attempt to convert the data to amounts of eumelanin or pheomelanin. I analyzed these data by various regression models and found no significant difference using all her raw data and various ratios and sums. However, when I analyzed these data for the ten red hair plus the albino hair sample for the ratio of PTCA/AHPs vs. the sum of PTCA plus AHPs I found a highly significant quadratic fit with an R^2 of 0.85 using the natural log of the ratio vs. the sum of PTCA plus AHP's.

I then looked at the six non-red hair samples and arbitrarily assigned a color factor of 1–6 for hair darkness with black as 6, dark brown as 5, brown as 4, Blonde as 3, light blonde as 2, and albino as 1 and found a highly significant relationship between this arbitrary color factor and the sum of AHPs plus PTCA (linear model $p = 0.0007$; $R^2 = 0.958$; RMSE = 23.94 and quadratic model $p = 0.0018$; $R^2 = 0.985$; RMSE = 16.339).

These statistical analyses suggests that for regression models for natural hair color based on the degradation products for eumelanin and pheomelanin it is better to separate black-brown-blonde hair from red hair. One reason is that the multiplying factors for the different markers for eumelanin and pheomelanin are too different and interfere with comparisons between red and non-red hair samples.

Napolitano et al. [129] suggested four basic types of pigmentation for human hair based on degradation criteria:

Eumelanic Type I (PTCA 100–300 ng/mg)
Eumelanic Type II (PTCA 50–100 ng/mg)
Pheomelanic Type I (BTCA 1,000–2,500 ng/mg and TTCA 200–250 ng/mg)
Pheomelanic Type II (TTCA 100–300 ng/mg)

From their data, the eumelanic type I hair covers black, dark brown and brown and distinguishes that group from the blondes and the many different reds. Pheomelanic type I cover the deep and dark reds and is distinguished from the other types primarily by BTCA providing values from 1,000 to 2,500 ng/mg of pheomelanins. The other two types do not appear to be as clearly distinguished.

Panaella and Napolitano et al. [146] published a newer method suggesting simultaneous determination of PTCA and BTCA as markers for eumelanin and pheomelanin which is worth exploring. See Chap. 3 for a discussion on the Genetics of hair pigmentation in the section entitled, *Hair Pigmentation and Genetics* which helps to explain some of the color differences in hair.

5.6.9 Chemical Oxidation of Hair Pigments

Wolfram and co-workers [12, 147] studied the oxidation of human hair with and without pigment. They also studied the oxidation of melanin granules isolated from human hair. These scientists found that hair with pigment degrades hydrogen peroxide at a measurably faster rate than hair without pigment. Since melanin

represents about 2% of the hair, this result suggests a faster rate of reaction of peroxide with hair pigment than with hair proteins.

For the reaction of peroxide with hair containing no pigment vs. hair containing pigment, the initial reaction rates are similar (through 10 min). However, longer reaction times (30–90 min) produce markedly different reaction rates. The initial rates, due to reaction with the surface and cuticle layers are expected to be similar, since pigment is not in the cuticle. However, as the reaction continues and the pigment becomes involved, peroxide is degraded faster by the pigment-containing hair.

Treatment of isolated melanin granules (from hair) with a large number of reagents (at different pH values) including thioglycolic acid, persulfate, permanganate, or perchlorate failed to provide detectable physical changes in the granules. However, treatment of the granules with alkaline hydrogen peroxide produces disintegration and dissolution of the granules. Wolfram also found that the pH of dissolution is at a maximum near the pK of hydrogen peroxide (pH 11.75). Furthermore, the dissolved pigment produces an intensely colored solution that fades on further reaction.

Wolfram [147] examined the effects of different oxidizing agents on their ability to decolorize soluble melanin and found the following order of efficiency: permanganate > hypochlorite = peracid > peroxide. This finding suggests that the melanin pigments within the granules are not accessible to most oxidizing agents. Furthermore, the granules must be degraded perhaps even solubilized before extensive decolorization of the pigment chromophore can occur. The first step (dissolution of the pigment granules) is a relatively specific reaction requiring oxidation at specific sites. Hydrogen peroxide is not as strong an oxidizing agent as permanganate or peracetic acid, but it is actually more effective for dissolving the granules than either of these other two oxidizing species. Once the granules are dissolved, reactions to degrade the chromophoric units of melanin can proceed more readily. Since the melanin chromophoric units contain many different sites susceptible to oxidation, the rate of the second step (degradation of the pigment chromophore) proceeds faster with the stronger oxidizing agents—e.g., permanganate > hypochlorite = peracid > peroxide—which is the order for decolorization of the solubilized melanin.

Although persulfate is not a stronger oxidant than hydrogen peroxide, mixtures of persulfate and peroxide provide a more effective bleaching system than peroxide alone. Martin [148] studied the persulfate oxidation of fungal melanins. He determined that persulfate is a selective oxidizing agent, releasing only those portions of melanins containing primarily fatty acids and phenolic compounds. Persulfate and peroxide are both somewhat selective in their attack on melanins. Presumably, peroxide attacks different portions or sites on the melanin macromolecules that facilitates solubilization of melanin so that the more potent persulfate can degrade it in solution. Thus, one might conclude that persulfate and peroxide complement each other in terms of their ability to bleach melanin pigment and therefore to bleach human hair.

Wolfram and Hall [147] also isolated several products from the reaction of alkaline hydrogen peroxide with melanin pigments, including proteinaceous species up to 15,000 daltons. These scientists further developed a procedure for the isolation of melanoprotein and determined the amino acid composition of melanoprotein from East Asian hair. They found fewer cystine linkages in melanoprotein than in whole fiber and a larger percentage of ionizable groups—i.e., approximately 35% more dibasic amino acid residues and 15% more diacidic groups.

Wolfram and Albrecht [149] concluded that hue differences in hair not only result from chemically different pigments, but also from differences in the degree of aggregation and dispersion of the eumelanin pigment. Both eumelanin and pheomelanin pigments contain polypeptide chains with similar amino acids as shown by Arakindakshan Menon et al. [150]. The red hair melanin contains more sulfur (as 1,4-benzothiazine units) than the brown-black melanins.

There are undoubtedly several similarities with regard to the chemical bleaching of eumelanins and pheomelanins. Wolfram and Albrecht [149] suggested that pheomelanin in hair is more resistant to photodegradation than the brown-black eumelanins. The more recent study by Hoting and Zimmermann [50] demonstrated that light-brown hair containing a mixture of pheo- and eumelanins is affected by all segments of light including visible light, whereas eumelanins are more photostable. These scientist examined degradation to the granules gravimetrically and by examining the polymers by infrared spectroscopy. The aromatic rings of both melanic structures are of high electron density, and consequently are both sensitive to attack by oxidizing agents, as demonstrated for the brown-black melanins. The eumelanin in addition provided greater protection to the proteins of hair than pheomelanin. Takahashi and Nakamura [151] studied the photolightening of red and blonde hair in both UV and visible light and their results are described below.

5.6.10 Photochemical Degradation of Melanins

Photochemical degradation of hair proteins occurs primarily near 254–350 nm, the primary absorbance region of un-pigmented hair as shown by Arnaud [58] and by Hoting, Zimmerman and Hocker [152]. Although several amino acids are degraded by light, the primary degradation occurs at cystine and thioester. Launer [60] and Inglis and Lennox [61] have provided evidence for photochemical degradation to other amino acids including methionine, histidine, tryptophan, phenylalanine, and leucine.

The mechanism for photochemical degradation of cystine is believed to involve both C–S and S–S fission mechanisms (see the section on photochemical degradation of hair proteins described earlier). Hair pigments function to provide some photochemical protection to hair proteins, especially at lower wavelengths, where both the pigments and the proteins absorb light (254–350 nm). Hair pigments

accomplish this protection by absorbing and filtering the impinging radiation and dissipating this energy as heat wherein virtually no damage occurs to the pigments. But above some energy level of excitation the ability of melanin to convert all of its absorbed energy to heat fails resulting in damage to its structure and chemical degradation.

Eumelanin ring opening may result from either ionic (chemical degradation) or free-radical reaction (photochemical degradation). Slawinska and Slawinski [153] suggested that these two mechanistic schemes may have some common intermediates. The ionic pathway probably begins by nucleophilic attack of the peroxide anion on the o-quinone group. Slawinska and Slawinski suggest that photochemical degradation of melanin occurs through a similar peroxide intermediate.

The first steps in the photochemical degradation of the eumelanin chromophore probably involves excitation to a radical anion and then attack by the oxygen radical anion on the o-quinone group, see Fig. 5.31. Ring opening of the six-membered ring indolequinone species then follows.

A related scheme may be involved for the photochemical degradation of pheomelanins.

Sarna et al. [154] concluded that pheomelanins are very similar to eumelanins with regard to their susceptibility to photooxidation. However, Arakindakshan Menon et al. [150] suggested that pheomelanins are more easily induced to an excited state than eumelanins. But, Wolfram and Albrecht [149] presented evidence that eumelanins are more sensitive to photochemical or chemical degradation than pheomelanins. And Hoting et al. [152] showed that the pigment of light-brown hair is affected by UV-A, UV-B and visible light, but eumelanins are more stable to light and provide a greater photoprotective effect.

Takahashi and Nakamura [151] clarified these seemingly disparate views on the relative photochemical degradation of pheomelanin and eumelanin by comparing the relative degradation of the pure pigments and the relative degradation of the pigments in hair. Both visible and UV light degrade pheomelanin in red hair, but

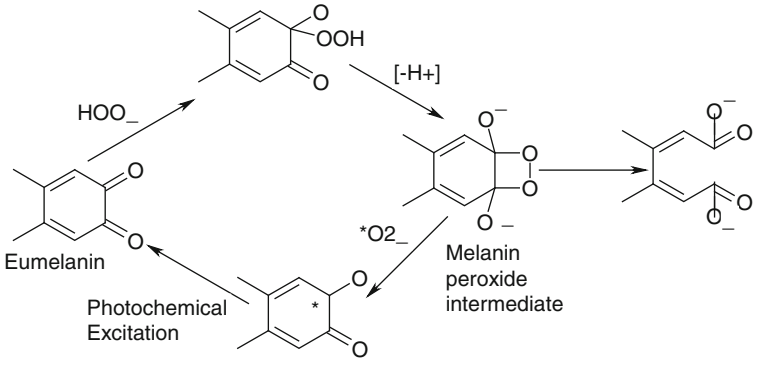


Fig. 5.31 Proposed mechanisms for degradation of melanins [153]

eumelanin in the hair fiber has been described as being more sensitive [149]. On the other hand, studies with isolated pheomelanin vs. eumelanin show that for the pure pigments pheomelanin is more sensitive to UV light than eumelanin [151]. This difference was proposed by Takahashi and Nakamura who observed the consequences of light acting directly on the pigments whereas in the fiber the light is attenuated by absorption and reaction with hair proteins producing radicals that react with the pigments.

Takahashi and Nakamura [151] also observed that blonde hair contains more eumelanin than pheomelanin and unlike red hair when exposed to UV light does not lighten until it is washed with water after irradiation. These scientists suggested that the washing or water effect may involve the hydroxyl free radical which may be required to be above a certain concentration to decompose eumelanin.

5.6.11 Photoprotection of Hair

Pande et al. [155] demonstrated that hair dyes (both oxidation and semi-permanent) grant a photoprotective effect to hair proteins providing a significant decrease in cortical damage. This protection shows up in tensile testing and the effect is greater the darker the dyes used. Meinert et al. [156] examined several commercial antioxidants for their sun protection properties in both pre-sun and after-sun hair products. White tea extract and Provitamin A when applied to hair in a pre-sun base formulation (at 0.05%) and then exposed to UV plus Visible light offered a higher tensile breaking stress than the same pre-sun base formulation without antioxidants. The other antioxidants produced either no significant difference or a lower tensile value. Less color change and lightening of non-dyed hair was observed with the pre-sun base plus White Tea Extract. The damage to the hair proteins was greater at higher radiant flux or lower relative humidity.

Schlosser [157] concluded that certain silicones, namely resins like trimethylsiloxysilicate or propylphenylsilsesquioxane are able to protect dyed hair (permanent dyed hair) from color change induced by UV radiation. However, silicones like dimethiconol/dimethicone did not show such an effect. Schlosser claimed that it is possible to reduce color facing both by wash-out and from UV radiation by adding silicones to the formulation of permanent and semi-permanent hair dyes.

5.6.12 Summary of Some Physical Properties of Bleached Hair

The gross or bulk chemical changes produced in hair by oxidation reactions including bleaching have been described in the previous sections of this Chapter. Details of changes in the breakage, stretching, bending, swelling and other physical properties are described in Chaps. 9 and 10.

5.7 Safety Considerations for Hair Bleaches

The primary safety concerns with hair bleaches, as with most hair care products, arise from misuse or failure to comply with the usage instructions. Skin irritation, hair breakage, oral toxicity, sensitization and scarring alopecia either have been reported from use (misuse) of hair bleaches or are mentioned on the warning labels of these products.

Bergfeld [158] has reviewed adverse effects of hair cosmetics recorded at the Cleveland Clinic Dermatology Department over a 10-year period. Effects attributed to hair bleaches were simple skin irritation and hair breakage. However, Bergfeld reported neither sensitization reactions nor complex toxic symptoms for hair bleaches.

Bourgeois-Spinasse [159] indicates a few incidents of allergic manifestations caused by ammonium persulfate powder; however, most hair bleaches today use potassium persulfate as the primary bleach accelerator. Bergfeld [158] reported permanent hair loss following misuse of hair bleaches and attributed it to scarring alopecia, although Bergfeld did not specify the extent of hair loss observed. Bergfeld concludes that side effects from hair bleaches are minimal, if the consumer is aware of damaged hair, any inherent skin disease and complies with the product usage instructions.

Treatment combinations are oftentimes more damaging to hair than one might expect. For example, extensive sunlight exposure in combination with chemical bleaching or chemical bleaching plus permanent waving must be done very carefully because of the compound damage provided by these combined treatments.

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Chapter 6
Interactions of Shampoo and Conditioner Ingredients with Hair

Abstract Shampoos and hair conditioners function primarily at or near the fiber surface. The primary function of shampoos is to remove soils or dirt from the hair surface, however, hair soils are highly varied from oily to particulate and the mechanisms for removal of these different soils also differ. Secondary functions of shampoos are also varied from conditioning the hair to dandruff control. With increasing damage to hair whether by chemical or photochemical reactions or even by abrasion, the hair surface becomes more hydrophilic and more acidic or anionic in character thus changing the affinity for different ingredients. Shampoos are often perceived as products that do not damage the hair; however damage can occur from some shampoos and such damage is described in detail. Different types of tests from laboratory to half head to tests on consumers are employed to evaluate the functionality of shampoos. These tests are described in detail with contrasts and some useful conclusions and insights. The sorption of shampoo and conditioning ingredients to hair including theories of sorption and diffusion are described in detail. Dandruff including scalp flaking, and skin irritation by surfactants is described in the last part of this chapter.

6.1 Introduction

For this edition, I have summarized some constructive research over the past 10 years that has expanded our understanding of the hair fiber surface layers and how these layers change as a function of chemical treatment and by shampooing, all of which is vital to understanding the interactions of shampoos and hair conditioner actions on this important region of the fiber. We have learned that both bound and free lipids are important to the surface layers. With increasing chemical or photochemical oxidation the surface and the isoelectric point of the hair decreases. These effects not only decrease hydrophobicity of the surface, they increase the surface acidity. At the same time, they damage the surface making it more susceptible to further damage by routine hair grooming actions.

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Our understanding of the structure of the cell membrane complex has also increased. Consequently, we have increased our understanding of how hair fibers are damaged from primary chemical treatments and grooming actions. More specifically, we've learned more about how hair fibers break and split during grooming, as described in this chapter and in more detail in Chap. 10. Hopefully, this knowledge will enable us to create new hair products and techniques that will decrease hair damage and breakage and will provide improved benefits to consumers.

According to legend, the word "shampoo" is derived from a Hindustani word meaning "to squeeze". Shampoos have a long and varied history. However, hair conditioners were not widely used until the mid-twentieth century following the introduction of "cold" permanent wave type products that exacerbated combing problems and damaged the hair.

The primary function of shampoos is to clean both the hair and the scalp of soils and dirt. While the primary function of hair conditioners is to make the hair easier to comb. Secondary benefits such as preventing flyaway hair, improving "hair shine", protecting the hair from further damage and improving hair feel are also important functions of hair conditioners. Shampoos also have important secondary functions such as dandruff control, mildness (baby shampoos), and conditioning (including both the primary and the secondary functions of conditioners). Conditioning functions have become even more important to shampoos with the use of silicones and cationic polymers in these products (see Chap. 8). Even fragrance character, impact and preference have created new market segments and become primary reasons for some consumers to purchase shampoos and conditioners.

Shampoos and hair conditioners have generally been perceived as products that do not damage hair. However, there is increasing evidence that these products, particularly shampoos can contribute to hair damage through abrasive/erosive actions combined with cyclic actions involving bending, compression and extension, both during and after the shampoo process. These actions produce degradation of both the keratin and the important non-keratin components of the hair surface, the cell membrane complex and the cuticle layers. Some new and important evidence for the mechanism(s) of these actions has been uncovered during the past several years and a detailed discussion of this subject appears in Sect. 6.9.1.

For hair conditioning products the principle function involves combability. Ease of combing depends primarily on lubrication of the fiber surface. This action is accomplished by the sorption or binding of lubricating or conditioning ingredients onto the hair surface. Thus, the most important interactions for both shampoos and conditioners are those that occur at or near the fiber surface or near the first few cuticle layers. Of course, if the hair surface is damaged to the extent that the cortex is exposed (near the tip ends) then shampoos and conditioners interact with exposed cortex too.

The first section of this chapter is concerned with shampoo and conditioner formulations and procedures to make these products. The control of product viscosity and important parameters concerned with product stability for shampoos,

hair conditioners and other types of hair care products are also discussed. The second section describes the different types of soil found on hair; soil origin and the ease or difficulty in soil removal. Methods to evaluate hair cleaning, the perception of hair cleaning, and shampoo lather as it relates to cleaning are then described. The next section is concerned with the attachment and the affinity of surfactant/conditioning-type molecules to hair including theories of sorption considering both surface adsorption and whole-fiber studies including fiber diffusion. Diffusion or penetration of chemicals into hair is more concerned with permanent waves, hair straighteners and hair dyes. However, due to the recent evidence that shampoos over time can damage the non-keratin pathways for entry into hair and more recent evidence that some conditioner-shampoo interactions can damage the cell membrane complex, diffusion is also important to shampoos.

The section on damaging effects to hair caused by shampooing and rubbing and stretching actions as occur in hair grooming during shampooing, drying, combing and brushing and styling of hair has been expanded by some new and exciting studies in this important area. At the end of this chapter is a brief introduction into the subject of dandruff and scalp diseases including causes and cures followed by a brief introduction into the subject of toxicity with special emphasis on mildness of surfactants to skin. This section includes a mathematical model to predict skin irritation by surfactant compositions with examples for a few shampoos.

6.2 General Formulation for Shampoos and Conditioners

Shampoos consist of several types of ingredients generally containing many of the following types of components:

- Primary surfactant for cleaning and foaming
- Secondary surfactant for foam and/or viscosity enhancement
- Viscosity builders: gums, salt, amide
- Solvents/hydrotropes to clarify the product or to lower the cloud point
- Conditioning agents
- Opacifier for visual effects
- Acid or alkali for pH adjustment
- Colors (D&C or FD&C colors) for visual effects
- Fragrance
- Preservative
- UV absorber usually for products in a clear package
- Specialty active ingredients, e.g., antidandruff agents, conditioning agents, etc.

Hair conditioners on the other hand are very different compositionally from shampoos. These are usually composed of several of the following types of ingredients:

- Oily and/or waxy substances including mineral oil, long chain alcohols and/or triglycerides or other esters including true oils and waxes, silicones and/or fatty acids
- Cationic substances consisting of mono-functional quaternary ammonium compounds or amines or even polymeric quaternary ammonium compounds or amines
- Bridging agents to enhance the adsorption of hydrophobic ingredients to the hair
- Viscosity builders
- Acid or alkalies for pH adjustment
- Colors and Preservative

Specific ingredients used in shampoos and conditioners and formulations for different types of products will be described in the next sections in this chapter after discussion of ageing, color stability, microbial stability and viscosity control in shampoos and conditioners.

6.2.1 Aging/Temperature Stability

There are no standard aging or stability tests in the cosmetic industry. Each company or independent formulator has developed its/his or her own set of standards to assess product stability to higher temperatures and each uses high temperature aging as a means to project longer term aging effects. The best approach is to test product at multiple temperatures because in some cases, e.g., some emulsions can be more stable at a higher than at a lower temperature.

Freeze thaw or temperature cycling is also important, especially in temperate or colder climates. This property is important because, we must know if the product is frozen or taken to a lower temperature will a phase change occur when the product is taken back to room temperature. In other words, will the appearance and product performance be restored? If precipitation or a permanent phase change occurs at lower temperatures, sometimes such problems can be addressed by improving the solvency of the system by adding solvents, or even by adding fluoride salts, hydrotropes, urea or other solubilizing additives.

The aging conditions of Table 6.1 are useful to evaluate a hair care product prior to sale. Obviously, in many cases one cannot afford to wait 1 year for completion of aging studies to go to market. In such cases, 3–6 months of satisfactory aging under the above conditions is helpful to make a judgment about product stability, especially if one has additional longer term aging data with related formulations.

I also recommend aging the product both in glass and in the actual package that the product is to be sold in. If this is done, then if an aging problem arises, one can determine if the problem is in the formulation itself, or if the formulation is reacting with the packaging material.

Table 6.1 Useful aging conditions for hair care products

Temperature aging (°C)	Time
50° (122°F)	3 months
40° (104°F)	3–6 months
25° (77°F)	1 year
25° (77°F)	In sunlight (if clear pkg.)
5° (40°F)	3 months
−20° (−4°F)	Freeze/thaw (lower temperatures if needed)

6.2.2 Color Stability

Color instability can be caused by several factors, such as the degradation of color additives or through chemical interaction of formula components, or with trace contaminants of components, or by ultraviolet radiation. This section is concerned with the latter problem involving stabilization of the system to light radiation.

For hair products that are sold in a clear package, light stability is often a major concern. For example, exposure to light may cause the dyes in the product to fade, fragrance components may degrade in the presence of light, or other additives may fade or decompose when exposed to light radiation. From chemical structures, a common source of this problem is unsaturated groups of a light sensitive component.

The easy solution is to use an opaque container; however, this solution may not be compatible with the marketing plan. An alternative is to add ultraviolet absorbers to the product. These absorb degrading radiation and thus inhibit, retard or prevent product degradation. Benzophenone-2 or Benzophenone-11 is usually the preferred agent, because of their broad spectrum protection, see Table 6.2:

Benzophenone-2 is usually preferred over benzophenone-11 because it is a single component, whereas benzophenone-11 is a mixture of benzophenone-6, benzophenone-2 and other tetra-substituted benzophenones. Most of these ultraviolet absorbers can be used in the vicinity of 0.05–0.2% concentrations for protection against degradation by ultraviolet light.

6.2.3 Preservation Against Microbial Contamination

Preservation of consumer products against microbial contamination is important because such contamination can lead to product degradation. However, in the worst case scenario it can lead to the spread of disease. So it is necessary to preserve consumer products against microbial contamination at the time of manufacture and to ensure the product is preserved for a reasonable time thereafter.

Some formulations are inherently more difficult to preserve than others. In general, the more water in a product the more difficult it is to preserve. In addition, some ingredients are more difficult to preserve against bacterial contamination than

Table 6.2 Preferred agents for sunlight protection of hair products

	Most effective wavelength (nm)
Benzophenone-2	290–350
Benzophenone-4	285
Benzophenone-8	355
Benzophenone-9	333
Benzophenone-11	290–355

others. For example, plant extracts, vitamins and some nonionic detergents are generally more difficult to preserve than other types of ingredients.

Formaldehyde, specifically formalin, is perhaps the single most effective preservative for shampoos and conditioners. However, because of its sensitization reputation, which actually occurs well above levels used in consumer products, it is not used in many countries. Sensitization by formaldehyde is not a problem if used at 0.1% or lower concentration in personal care products. In many cases it is used at 0.2% in household products. Most companies avoid the use of formaldehyde in baby products.

One convenient way to classify preservatives is as:

– Those that release formaldehyde and those that do not release formaldehyde

In the former group, we have Germaben II, which is one of the more effective preservatives, Germall 115, Germall II and Glydant. Germaben II is often used in shampoos and conditioners at a level of approximately 0.5% of the product. This preservative consists of a mixture of diazolidinyl urea (releases formaldehyde) and parabens in propylene glycol. Germall 115, another effective preservative, is actually imidazolidinyl urea, and can be made more effective by the addition of parabens. Approximately 0.05% methyl paraben and 0.1% propyl paraben is highly effective in the presence of this preservative. Germall II (diazolidinyl urea) is another effective preservative. It is not as effective as Germaben II, because it does not contain parabens as does Germaben II. Glydant is actually DMDM hydantoin and is often used in the vicinity of 0.5% of the product. It is another effective preservative. It too is made more effective by the addition of parabens.

Among the more commonly used preservatives that do not release formaldehyde are parabens, Dowicil 200 and Kathon CG. Kathon is effective at extremely low concentrations, about 15 ppm. A commonly used mixture of parabens consists of 0.1% methyl paraben and 0.7% propyl paraben. This mixture of parabens is moderately effective alone, but is more effective in combination with other preservatives. The European Economic Community (EEC) prohibits the use of parabens above 0.8%. Parabens like most phenolic preservatives are deactivated by nonionic surfactants; therefore, parabens should not be used in products containing high concentrations of nonionic surfactant like baby shampoos.

Dowicil 22, has the CTFA designation, Quaternium-15, and is sometimes used between 0.05% and 0.2% and can be used in combination with parabens to enhance its preservative capacity. Kathon CG, is a mixture of methyl chloroisothiazolinone

and methyl isothiazolinone, and is another useful preservative for the preservation of cosmetic hair products.

Benzyl alcohol, sodium benzoate, sorbic acid and even sequestrants such as EDTA are used as adjuncts for the preservation of hair care products. For example, EDTA is effective against pseudomonas, and should be considered in systems where pseudomonas could be a problem, but it should not be considered alone without the use of other preservatives.

6.2.4 Viscosity Control in Shampoos and Conditioners

To control the viscosity of many shampoos, salt is added to the surfactant system. The interaction between salt and long chain surfactants transforms the small spherical micelles of the surfactants into larger rod-like or lamellar or even liquid crystalline "type" structures that increase the viscosity of the liquid shampoo. If one plots the salt concentration versus the viscosity in such a system, one typically finds an optimum for the maximum viscosity, see Fig. 6.1. Above this optimum salt concentration, additional salt decreases the viscosity. In developing such a system in which viscosity is controlled by salt addition, it is preferable to select the appropriate salt concentration on the ascending part of the viscosity-salt concentration curve. Nevertheless, many light duty liquid products and some shampoos are formulated on the descending part of the curve. The selection of surfactant, amide and other components are critical to viscosity-salt concentration control in such a system. Furthermore, impurities such as salt contaminants in surfactants must be

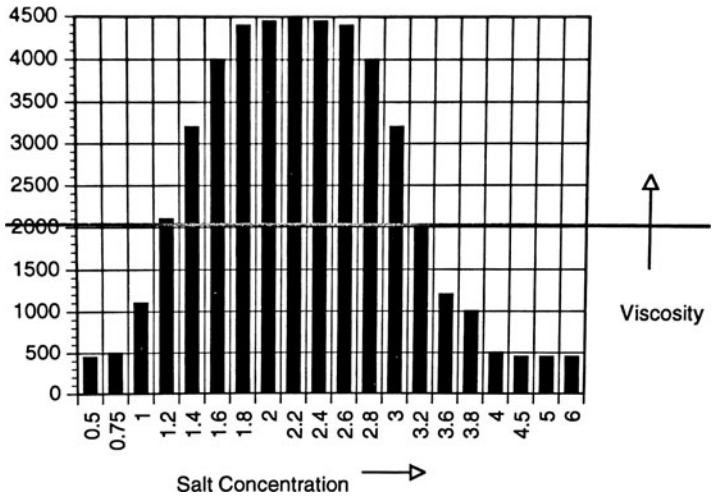


Fig. 6.1 The general relationship of the salt content to the viscosity in surfactant systems (shampoos)

carefully controlled to obtain the appropriate viscosity when salt control is employed.

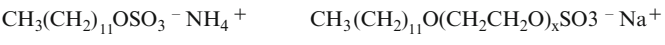
Polymeric gums such as methyl cellulose or hydroxy ethyl cellulose have also been used in shampoos to help control viscosity. Here, the polymers interact with the surfactants forming even larger more cohesive aggregates of higher viscosity. Alkanolamides interact similarly and are very effective in reducing surfactant head group repulsion, thereby allowing even larger and more cohesive aggregates of higher viscosity. Other polar surfactants such as betaines and amine oxides can interact similarly to help increase viscosity of anionic surfactant systems. In such systems, the salt concentration is also helpful to viscosity control.

Solvents such as propylene glycol, glycerine, carbitols or other alcohols are sometimes used in shampoos to help solubilize or to clarify product or to lower cloud-clear points. Such ingredients often tend to lower product viscosity and are sometimes used for this purpose alone.

6.2.5 Ingredient Structures and Making Procedures and Formula Examples for Shampoos and Conditioners

6.2.5.1 Shampoos

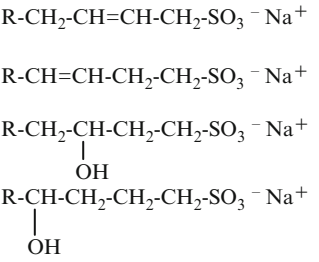
The main primary surfactant used in the United States for shampoos is ammonium lauryl sulfate, while in many other countries, sodium or ammonium laureth sulfate (with an average of 2 or 3 moles of ethylene oxide) is the current leader. These two surfactants are used alone or blended together for shampoos because of their fine ability to clean sebaceous soil, and perhaps even more importantly, because of their excellent lather and viscosity building properties. Sometimes, for product clarity reasons sodium lauryl sulfate and sodium laureth sulfate may be used.



Ammonium lauryl sulfate

Sodium laureth sulfate

Alpha olefin sulfonate has also been used to a limited extent in lower priced shampoos. This surfactant is represented by the following structures:



Alpha olefin sulfonate consists of a mixture of the above four surfactants in about equal quantities. The commercial shampoo material is 14–16 carbon atoms in chain length; therefore, R = 10–12 carbon atoms. Generally a carbon chain length of 12–14 carbon atoms or a coco type distribution of approximately 50% C12 is used for the primary surfactant in shampoos. This chain length provides excellent foam character, viscosity and cleaning. Longer or shorter chain length surfactants are used only in specialty systems.

Secondary surfactants are used as foam modifiers, to enhance cleaning or even for viscosity enhancement. The principle secondary surfactants used in shampoos are amides such as cocomonoethanolamide (cocamide MEA) the most common amide today while other amides have also been used. Betaines are also excellent foam modifiers. Cocamidopropylbetaine is the most popular betaine in shampoos and is becoming increasingly important as a secondary surfactant. Cocamidopropyl sultaine, cocamidopropyldimethylamine oxide and cocoamphoacetate and its derivatives have also been used as amphoteric surfactants in shampoos.

The pH of shampoos is usually adjusted with a common acid such as citric or even mineral acid. Buffers such as phosphate or other inexpensive materials are also used for pH control. Preservation against microbial contamination is necessary and is discussed above. A good cleaning shampoo (Table 6.3) will consist of at least one primary surfactant, such as an alkyl sulfate or ethoxy sulfate, or even olefin sulfonate, in combination with one or more secondary surfactants. Generally an acid such as citric acid for pH adjustment, a preservative, colors, fragrance and water are also necessary additives.

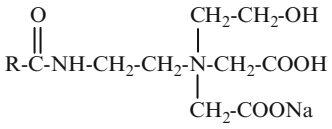
Baby shampoos (Table 6.4) and some light conditioning shampoos employ nonionic surfactants such as PEG-80 sorbitan laurate, PEG-20 sorbitan laurate or PEG-20 sorbitan oleate as the primary surfactant and amphoteric surfactants such as cocoamphocarboxyglycinate or cocoamidopropylhydroxysultaine are used as secondary surfactants to help improve the mildness of anionic surfactants and at the same time to improve cleaning and lather performance.

Table 6.3 Example of a clear cleaning shampoo

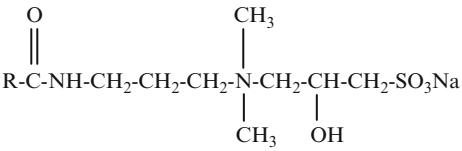
Ingredient	Percentage
Sodium laureth sulfate	8
Sodium lauryl sulfate	7
Cocamide MEA	2
Cocamidopropyl betaine	2
Glycerin	1
Fragrance	0.7
Citric acid	To desired pH
Sodium citrate	~0.2
Sodium chloride	To desired viscosity
Colors	To desired color
Sodium benzoate	As needed
Tetrasodium EDTA	As needed
Preservative (Kathon CG)	As needed
Water	q.s. to 100%

Table 6.4 Example of a baby shampoo

Ingredient	Percentage
PEG-80 sorbitan laurate	12
Sodium trideceth sulfate	5
Lauroamphoglycinate	5
Laureth-13 carboxylate	3
PEG-150 distearate	1
Cocamidopropyl hydroxysultaine	1
Fragrance	1
Preservative (Germaben II)	0.5
Colors	To desired color
Water	q.s. (to 100%)



cocoamphocarboxyglycinate



Cocoamidopropylhydroxysultaine

Conditioning agents for shampoos are varied and may generally be classified as lipid type, soap type or salts of carboxylic acids, cationic type including cationic polymers, or silicone type including dimethicone or amodimethicones, see structures below in Sect. 6.2.5.2. An example of a light conditioning shampoo is described in Table 6.5. Opacifiers such as ethylene glycol distearate, or soap type opacifiers are often used in conditioning shampoos. These additives provide visual effects, to promote the perception that something is deposited onto the hair for conditioning.

Two in one shampoos can be higher in conditioning than ordinary conditioning shampoos. These normally contain a water insoluble dispersed silicone as one of the conditioning agents. Conditioning shampoos containing water insoluble dispersed silicones are generally better for conditioning unbleached hair than other conditioning shampoos. But, silicone conditioning shampoos are not as effective for bleached hair because the hydrophobic silicone does not deposit readily onto the hydrophilic surface of bleached hair. The making procedure is also more complex for silicone containing shampoos and the particle size of the active ingredient is critical to its effectiveness. This type of system is also difficult to stabilize. The formula below (Table 6.6) is stabilized by a combination of the long chain

Table 6.5 Example of a light conditioning shampoo

Ingredient	Percentage
Ammonium lauryl sulfate	8
Sodium laureth-2 sulfate	6
Cocamide DEA	3
Polyquaternium-10	1
Sodium phosphate buffer	0.4
Fragrance	1
Ethylene glycol distearate	0.6
Preservative (Germaben II)	0.5
Sodium chloride (to adjust viscosity)	As needed
Colors	As needed
Water	To 100%

Table 6.6 Example of a 2 in 1 conditioning shampoo

Ingredient	Percentage
Ammonium lauryl sulfate	10
Sodium laureth-2 sulfate	6
Dimethicone	2.5
Ammonium xylene sulfonate	2
Glycol distearate	2
Cocamide MEA	2
Fragrance	1
Thickening gum (hydroxy ethyl cellulose)	0.3
Stearyl alcohol	0.3
Preservative (Germaben II)	0.5
Colors	As needed
Water	To 100%

acylated agent, e.g., glycol distearate and the thickening gum. Although, Grote et al. [1] describe thickeners as optional components, in our experience with this type of acylated suspending agent, thickeners are essential to long term product stability.

An Introduction into Making Procedures for Clear Shampoos and Emulsion Products

The simplest making procedure is for a clear solution product, where no gums or water insoluble solids are in the formulation. In this case, heat is usually not required to make the product. This procedure may be considered as consisting of four steps.

1. Dissolve the surfactants in water with stirring. Note the order of addition may be important. In general, add the foam modifier last.
2. Add the fragrance, color solutions and preservative and stir until a uniform solution is obtained.

3. Adjust the pH with either acid or alkalinity.
4. Add salt for the final viscosity adjustment.

Note, whenever possible the final step in product manufacture should be viscosity adjustment to allow for optimum mixing and for maximum energy conservation. It may be useful or necessary to dissolve the fragrance or an oily component in a small amount of concentrated surfactant prior to adding it to the aqueous phase.

If solid amides are used as foam modifiers then heating, above the melt, may be necessary to either dissolve or emulsify such an ingredient. If gums are used, it may be necessary to dissolve the gum in a small amount of water prior to adding it to the detergent phase. In any case, when polymeric gums are used one should consult and follow the gum manufacturer's directions for dispersing/solubilizing the gum into the formulation.

Most conditioners and conditioning shampoos (such as 2 in 1's) are oil in water emulsions and are more complex to make than the simple clear shampoo just described. The following procedure can be used to make most oil in water emulsion products:

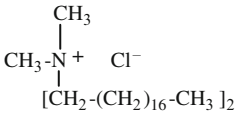
1. Dissolve the water soluble ingredients in deionized water while stirring and heat if necessary. This is part A.
2. If necessary, heat the oil soluble components to melt the solids. These ingredients may be added together or separately. The order of addition is often critical. This is Part B. When adding Part B or its components to part A; heat part A to approximately 10° above the melting point of the solids. Add Part B or its components to part A while stirring.
3. Continue stirring for at least 10–15 min and then add the remaining water.
4. Cool and add the preservative, fragrance and colors.
5. Adjust the pH and then the viscosity.

The speed of agitation, type of mixer, rate of cooling and order of addition are all important to produce consistent emulsion products that are stable and provide high performance. In the case of 2 in 1 shampoos with water insoluble silicones, the silicone will generally be added after the fatty components, once the emulsion has been formed. Three examples of hair conditioner formulations and their making procedures are described in the next section. These should provide a better feel for how to make and formulate emulsion hair products than the general outline above.

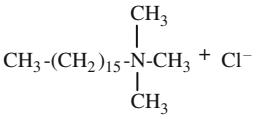
This discussion is obviously a cursory introduction into shampoo and conditioner making procedures. For more details on emulsions, their structure, stability and formation, see the review by Eccleston [2] and the references therein. For additional details on the making of shampoos and conditioners, consult formularies [3] and recent literature from cosmetics courses such as offered by "The Society of Cosmetic Chemists," and "The Center for Professional Advancement." For additional details on product compositions, consult references [1–3], product ingredient labels, and the books by Hunting [4, 5].

6.2.5.2 Hair Conditioners

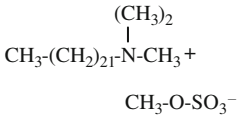
Creme rinses and most hair conditioners are basically compositions containing cationic surfactant in combination with long-chain fatty alcohol or other lipid components. Distearyldimonium chloride, cetrimonium chloride, stearalkonium chloride and behentrimonium methosulfate are typical cationic surfactants used in many of today's hair conditioning products. Amines like dimethyl stearamine or stearamidopropyl dimethylamine are other functional cationics used in these products. Cationic polymers such as Polyquaternium-10 (quaternized cellulosic) and Polyquaternium-7 (co-polymer of diallyl dimethyl ammonium chloride and acrylamide) are also used (more in shampoos than in hair conditioners). Care must be taken to avoid build-up on hair when formulating with cationic polymers. See the section on cationic polymers in hair products in Chap. 8 and Sect. 6.3.4.8 in this chapter.



Distearyldimonium Chloride

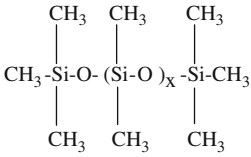


Cetrimonium Chloride



Behentrimonium Methosulfate

Typical lipids used in these products are cetyl alcohol and/or stearyl alcohol, glycol distearate or even silicones like dimethicone, amodimethicones, and dimethiconols. See the section on silicones in Chap. 8.



Dimethicone

For additional details on product compositions, consult references [1–3], product ingredient labels, and the books by Hunting [4, 5].

6.2.5.3 Some Hair Conditioner Formulations and Making Procedures

An example of a good simple, yet effective formulation for a creme rinse/conditioner is described in Table 6.7.

The making procedure for this type of hair conditioner is the one described for oil in water emulsion, conditioning shampoos.

If one examines conditioners in the marketplace one also finds more complex conditioners, many that are different for the sake of using ingredient names rather

Table 6.7 Example of a simple hair conditioner

Ingredient	Percentage
Cetrimonium chloride	1.0
Cetyl alcohol	2.5
Thickening gum (hydroxy ethyl cellulose)	0.5
Fragrance	0.2
Preservative (Germaben II)	0.5
Water	q.s.

Table 6.8 Example of a more complex hair conditioner

Ingredient	Percentage
Cetyl alcohol	1
Stearyl alcohol	1
Hydrolyzed animal protein	<1
Stearamidopropyl dimethyl amine	<1
Cetearyl alcohol	<1
Propylene glycol	<1
Keratin polypeptides	<1
Aloe	<1
Chamomile	<1
Tocopherol	<1
Panthenol	<1
Preservative	<1
Colors	<1
Fragrance	<1
Water	q.s. (to 100%)

than for real product performance. An example of such a product is described in Table 6.8.

This "kitchen sink" hair conditioner would be made according to the same procedure described above for making oil in water emulsion conditioning shampoos. Hype compounds like proteins, placenta extract, vitamins (tocopherol), provitamins (panthenol), etc. that are almost always nonfunctional or less functional than a corresponding non-hype material are commonly used in hair conditioning products because of the consumer appeal of the ingredient name.

Deep conditioners may contain more oils or simply a higher viscosity; see the example of Table 6.9. To make this product, melt the oil phase, cetyl alcohol and stearamidopropyl dimethyl amine in the presence of mineral oil and propylene glycol and heat to 80°C. Add citric acid to water and heat to 80° as the quat is added to the aqueous phase. Add the oil phase (I) to the aqueous phase and stir for about 20 min; then cool and add the preservative, colors and fragrance.

Table 6.9 Example of a deep hair conditioner

Ingredient	Percentage
Part I: cetyl alcohol	6.0
Stearamidopropyl dimethyl amine	1.5
Mineral oil heavy	0.5
Propylene glycol	1.0
Part II: citric acid	0.2
Dicetyldimonium chloride	1.0
Germaben II	0.5
Fragrance	0.4
Water	q.s. to 100%

6.3 Cleaning Soils from Hair and Cleaning Mechanisms

Shampoos are formulated under several constraints; because a hair-cleaning system must contact the scalp. These constraints include the following: Cleansing ingredients must be safe, requiring low toxicity, low sensitization potential, and low skin and eye irritation potential. Low temperatures (20–44°C) are used during shampooing. Short cleaning or reaction times (minutes) are also employed. Low substantivity of detergent for hair is preferred, except for conditioning, where adsorption is necessary (see Sect. 6.6). Essentially no degradation of the hair substrate by the cleansing system is desirable. The cleansing system should be capable of removing a variety of different soils without complicating interactions between shampoo ingredients and the soils.

The most common test criteria used to assess cleaning efficiency of shampoo products relates to the amount of soil left on the hair surface after shampooing. However, the rheological and other physical properties of the soil have recently been shown to also be important. The condition of the hair surface is critical to cleaning. Damaged hair or weathered tip ends tends to reduce the chemical affinity of the hair surface to hydrophobic soils. However, cracks or crevices created by damaging actions provide cavities to trap soils rendering soil removal more difficult. Specific properties of hair fibers versus assemblies, attributes of the product (fragrance, lather, and viscosity), and the rate of re-soiling are also relevant to the perception of hair-cleaning efficacy. The next section of this chapter is concerned primarily with the different types of soil found on hair, their origins, and their removal by existing surfactant systems.

6.3.1 Hair Soils and Detergency Mechanisms

Hair soils may be classified as one of five different types:

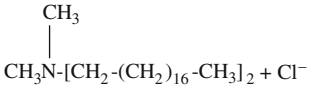
1. Lipid soils are the primary hair soil and are largely, but not entirely sebaceous matter. For a more complete description of the chemical composition of sebaceous soil, see Chap. 2.

2. Soils from hair products or hair preparations represent another important group consisting of a variety of different cationic ingredients, polymers, and lipophilic ingredients.
3. Metal ions and their derivatives (especially hardness ions) which include calcium bridged fatty acids, fatty alcohol sulfates and metals bound to cysteic acid residues.
4. Protein soils are from the skin, but probably in most cases do not constitute a serious soil removal problem.
5. Environmental soils vary consisting of particulate matter from air (hydrocarbons and soot) and minerals from the water supply.

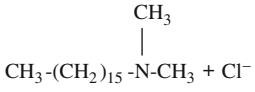
6.3.2 Soils from Hair Products

A variety of different soils from hair products may be found on hair surfaces. It is essential for a good shampoo to remove these soils without complicating interactions between the surfactant and the soil. Hair products provide lipid-type soils, cationic soils, polymeric soils, and metallic ions or fatty acids that can bridge metallic ions to hair.

Neutral lipids are found in many different types of hair products including some conditioners, pomades, men's hair dressings, etc. Monofunctional cationic ingredients such as stearalkonium chloride and cetrimonium chloride are the primary active ingredients of creme rinses and other hair-conditioning products. The increased usage of these products, over the last few decades makes this soil type even more common. In addition, use of dialkyl quaternary ammonium ingredients such as dicetyldimonium chloride, distearyldimmonium chloride or even longer chain-length quats such as behentrimonium methosulfate are becoming more common in hair conditioner usage.



Distearyldimmonium chloride



Cetrimonium Chloride

Cationic polymers such as polymer JR (Polyquaternium-10) a quaternized cellulosic ingredient [6], cationic guar, a quaternized polymer of galactose, Merquat polymers (Polyquaternium-6 and 7) copolymers of dimethyl diallyl ammonium chloride and acrylamide [7], and Gafquat polymers (Polyquaternium-11) (copolymer of polyvinyl pyrrolidone and dimethylaminoethyl methacrylate) [8] have all been used and are currently used in conditioning shampoos, setting lotions, or mousses. (See Chap. 8 for additional details regarding cationic polymers used in hair care products.)

Neutral and acidic polymers such as polyvinyl pyrrolidone, copolymers of polyvinyl pyrrolidone with vinyl acetate, and copolymers of methyl vinyl ether with half esters of maleic anhydride, etc. are all used in hair styling and hair setting products; see Chap. 8 for additional details. Fatty acids such as lauric, myristic, or palmitic have been used in conditioning shampoos, although these are used less frequently than in previous years. Fatty acids interact with calcium and magnesium and other ions of the water supply and deposit on hair. It is believed that at least part of this type of conditioning agent binds to the hair through metal ion bridges [9]. The greater the water hardness used in washing and rinsing the hair, the larger the amount of deposition of fatty-acid conditioner onto the hair surface (Schebece, private communication) from a shampoo. Thus the primary sources of calcium-bridged fatty acids on hair are conditioning shampoos and soap bar products that react with metal ions in the water supply. In moderate to high hard-water areas, fatty acids from sebum and free lipids in the surface may also be a source for metal ion-bridged fatty acid on the hair fiber surface.

6.3.3 Environmental Soils

Hair is an excellent ion exchange system. Metallic ions may be sorbed to hair in multiple forms such as lipids, e.g., calcium stearate or as particulates, e.g., metal oxides. Many metallic ions such as copper (+2) [10] can adsorb to hair, especially after frequent exposure to swimming pool water. It has been suggested that metallic ions such as chromium, nickel, and cobalt may bind to hair from swimming pool water [10] or even from some water supplies. Sorption of metallic ions like calcium or magnesium occurs even from low concentrations in the water supply rather than from hair products. However, fatty acids present in hair products and soaps enhance the adsorption of most of these metallic ions to the hair surface, as described above. Alcohol sulfates and even ether sulfates (least affected by metallic ions) can adsorb to the hair with metallic ions, but to less a degree than soaps. Heavy metals such as lead and cadmium have been shown to collect in hair from air pollution [11], and other metals like zinc, are available from antidandruff products, and deposit on and in the hair from the zinc pyrithione active ingredient.

Other soils that shampoos must remove are proteinaceous matter arising from the stratum corneum, sweat, and other environmental sources. We have already described metallic ion contamination from the water supply, from swimming pools, and sweat in Chap. 2. In addition, particulate soils from the environment include hydrocarbons, soot, and metal oxide particles, which should also be at least partially removed by shampoos.

6.3.4 *Detergency Mechanisms and Surface Energy of Different Hair Types*

6.3.4.1 Surface Energy of Hair

Surface tension is technically the property of a liquid and is an indication of the attractive forces between a liquid and another surface. The surface tension of hair generally describes the attractive forces between hair and the surface of water and is technically the surface energy, see the explanation in Table 6.10 for the units. Horr [14] has reviewed the literature on contact angle measurements of wool fiber and reported the surface tension for Merino wool fibers to vary over the range of 34 ± 4 mJ/m^2. But this value is high compared with values for human hair and therefore must be for oxidized wool. In most of these measurements, contact angles were measured using water as the polar probe and methylene iodide as the non-polar probe liquid.

The surface tension/energy of human hair from contact angle measurements has been shown by Yang [15] and others [12, 13] to vary from below 24 mJ/m^2 for conditioned hair to above 45 mJ/m^2, for damaged hair (not conditioned), see the data of Table 6.10 and the cited references. Alter and Cook found the values for human hair to be higher at low RH and lower at higher RH. For example these scientists found that virgin hair fibers ranged from 25 to 28 mN/m over the RH range and bleaching produced somewhat higher values that did not vary from 3 to 9 bleaching treatments. Alter and Cook also indicated in their paper that most hydrocarbon surfaces vary from 22 to 35 mN/m.

Kamath, Dansizer and Weigmann of TRI/Princeton [12, 16] used a liquid membrane wettability scanning method with water as the polar medium and methylene iodide as the non-polar medium and calculated surface tensions (numerically equal to surface energies) from the equation of Wu [16]. From the perspective of numerical directionality, the dispersive or non-polar component of the liquid

Table 6.10 Surface tension/energies[a] of hair by treatment

	Surface energy (mJ/m^2)[a]	Surface energy terms (mN/m)[a] [12]				
		σ_L^d	σ_L^-	σ_L^+	σ^{AB}	$\sigma^{Tot.}$
Virgin hair	~28 [12] 25–28 [13]	23.8	6.6	22.9	24.6	48.4
Conditioned hair	24–26 [12]					
Damaged hair	31–47 [12]					
Chemically bleached	28–30 [13]	30.4	5.5	37.6	28.7	59.1
Bleached plus conditioned	24–26 [12]	18.7	17.5	37.1	51.0	69.7
Permanent waved		25.8	2.2	39.2	18.7	44.5
UV irradiated		31.6	9.3	51.0	43.4	75.0

[a]Surface energy applies to solid and liquid surfaces and is generally expressed in mJ/m^2 (energy per unit area) while surface tension apples only to liquids and is normally expressed as mN/m (milli-Newton per meter) or force per unit length; numerically they are the same

surface energy (σ_L^d) of the data from TRI/Princeton is in line with the data from other laboratories of surface energies determined by other contact angle methods.

These data of Table 6.10 show that the hair fiber surface of undamaged hair "virgin hair" is very hydrophobic with a low surface energy. Furthermore, the hair fiber surface becomes more hydrophilic with increasing damage to the fibers (higher surface energy), especially with oxidative damage. This result is consistent with the fact that oxidation removes 18-methyl eicosanoic acid from the surface oxidizing the thioester and disulfide to higher oxidation states (primarily sulfonate). It also removes free lipids from the surface. Furthermore these data show that treatment of bleached hair with conditioners makes the hair surface more hydrophobic with a lower surface energy. Thus, the cationic part of conditioners binds to the hair surface by ionic bonds with the hydrophobic tails projecting into the air to provide a hydrophobic hair surface. Because hair conditioners are usually formulated with lipids like fatty alcohols and silicones these most likely bind to the hydrophobic tail of the cationics and make the hair surface even more hydrophobic.

6.3.4.2 Detergency Mechanisms

Although mechanical action is involved in cleaning hair, as a first approximation mechanical action during shampooing may be assumed to be constant for any given person. Therefore, detergency mechanisms are the most viable approach to improve hair cleaning. Detergency mechanisms [17] generally consider soils as either oily (liquid soils) or particulate (solid soils). Oily soils are the most common hair soil and appear as oily films of varying thickness and distribution on the hair fiber surface, see Fig. 6.2. The removal of oily soils involves diffusion of water to the soil-fiber interface and roll-up of the soil. Roll-up generally determines the rate of soil removal, although solubilization, emulsification, and soil penetration are also important. Roll-up of oil on a fiber surface is caused by interfacial tensions of (oil on fiber) $£_{fo}$, (water on fiber) $£_{fw}$,

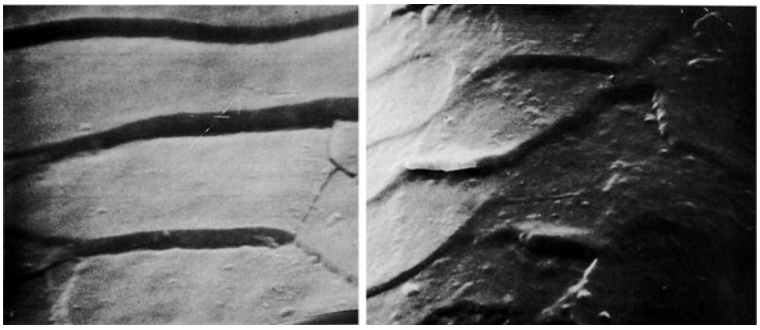


Fig. 6.2 Scanning electron micrographs hair fiber surfaces illustrating sebaceous soil (*Right*) versus a fiber cleaned with sodium lauryl sulfate solution (*Left*)

and between (oil and water) $£_{ow}$. When the combination of these interfacial tensions $\underline{R}$ is positive in the expression below the oily soil rolls-up:

$$\underline{R} = £_{fo} - £_{fw} + £_{ow} \times \cos \oslash$$

In other words, to produce oily soil roll-up, the detergent must make the fiber surface more hydrophilic [17]. Thus, the removal of lipid soil from hair is dominated by the hydrophilicity of the fiber surface. Anything that can be done to make the fiber surface more hydrophilic, such as bleaching or washing with anionic surfactants in water, should facilitate oily soil removal. This is one of the reasons why damaged hair, which is more hydrophilic at the surface than virgin hair (Table 6.10) is so sensitive to oil removal and often appears very dry (which is actually less oily rather than containing less water) after shampooing.

Since hair is more damaged, that is it contains less lipid and it is more oxidized at the tip ends than at the root ends, the fibers will be more hydrophilic at the tip ends [16]. Thus, surface bound hydrophobic soils should be more easily removed from the tips. This fact helps to account for the phenomenon of dry tips and oily roots on the same person. On the other hand, weathered tip ends of hair will have more raised scales and cracks and crevices to trap soils rendering them more difficult to remove from these aspirates on the fibers.

Solubilization of hydrophobic soils is perhaps equally important to roll-up for shampoo cleaning. Because of dilution with water, shampoos are generally used at 1–4% surfactant concentration, well above the critical micelle concentration (cmc). In addition, shampoos are actually mixed surfactant systems consisting of mixed micelles reducing the cmc of the system even further. Thus hydrophobic soils of sebum and other oily soils can be solubilized by being incorporated into the structure of the micelles of shampoos. Solubilization is a very important mechanism for cleaning oily soils from hair during the shampoo process.

Particulate soils arise from dust, dirt, soot, hydrocarbons, metal oxides and even from hair products that deposit materials such as silicas or aluminas or titanium oxide from about 1 μm to less than 0.1 μm particle size, see Fig. 6.3. The removal of particulate soil is not controlled by the hydrophilicity of the fiber surface. Particulate soil removal depends on the bonding of the particle to the surface, the location of the particle [17], and the size of the particle. Particle size is perhaps the most critical variable for the removal of particulates. As the particle size decreases the area of contact with the fiber surface increases making it more difficult to remove. At particle sizes of less than 0.1 μm, it is very difficult to remove material from hair surfaces by ordinary shampooing [18]. When the soil particle consists of non-polar components, its adhesion depends mainly on Van der Waals forces. Therefore, with waxes or polymeric resins, the molecular size and shape are important to their removal. Unless unusually high molecular sizes are involved, the removal of such soils is oftentimes easier than for cationic polymers where adhesive binding includes a combination of ionic and Van der Waals forces.

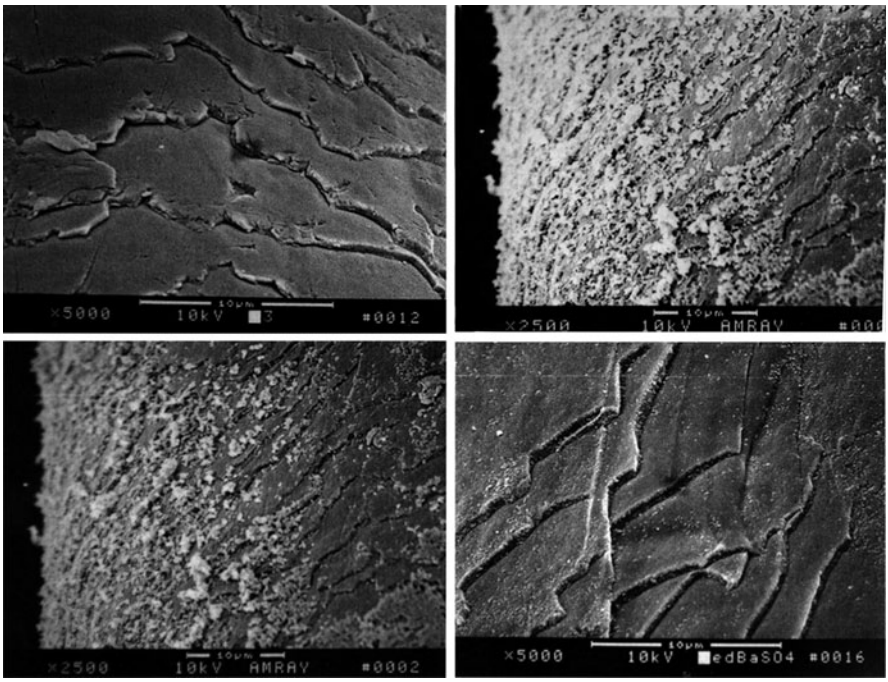


Fig. 6.3 Particulates on the surface of hair fibers. *Upper left*: control fiber with clean surface. *Upper right*: Barium sulfate particles on the surface. *Lower left*: Black iron oxide particles on the surface. *Lower right*: Precipitated fine Barium Sulfate on the hair surface

When hair soils fit into these two distinct classes (oily or particulate) the mechanism for their removal is easy to understand. However, other soils (e.g., conditioners containing cationic surfactant plus oily substances or some plasticized resins) are intermediate in classification and their removal probably involves either a combination of mechanisms or a more complicated cleaning mechanism.

6.3.4.3 Methods to Evaluate Clean Hair

Several methods have been described to evaluate the ability of different shampoos or detergents to clean soil from the hair [10, 19–27]. Most of these methods have been developed to evaluate the removal of lipid soil from the hair [19, 21, 22]. Some of these methods are soil specific [21] or are more sensitive with specific soil types [24], while others work for most soils [23].

Hair cleaning methods may be classified according to the following categories: chemical and physical properties, microscopic methods, or subjective or sensory evaluation procedures. Chemical or physical methods may involve either direct analysis of the hair itself [23] or analysis of hair extracts [20, 21]. For direct analysis of hair, chemical methods such as ESCA (XPS) [25] or infrared spectroscopy may

be used. Physical methods such as fiber friction [24] or light scattering [23] or examination of inter-fiber spaces, on the other hand, are less soil-specific than chemical methods and offer the ability to look at a variety of soil types, but sometimes these methods are less discriminating.

Microscopic methods have been used to evaluate hair cleanliness [20]. However, sensory evaluation of hair greasiness on hair swatches [26] and subjective assessments from half-head and consumer tests are also useful. The latter evaluations are in a sense the "final word" in the estimation of cleanliness by shampoos. Most procedures involve evaluation of either single soils (primarily hair lipid) or short-term effects of different products. One area of concern that has received relatively little attention is long-term effects that might result from gradual buildup or from gradual interactions between different hair products such as silicone containing products or between hair lipid and different hair products. This area will become increasingly important for future research for shampoos as new substantive conditioning agents are discovered and employed.

6.3.4.4 Cleaning Efficiency of Shampoos

To evaluate shampoo efficiency, one must consider the different soil types separately and then together. We must also learn to distinguish between cleaning soil from the hair and the deposition of ingredients from the shampoo formulation itself.

6.3.4.5 Cleaning Lipid Soil from Hair

For efficiency in removing lipid soil from hair, the literature does not provide a consensus. For example, Shaw [20] concludes that a one-step application of anionic shampoo removes essentially all the hair-surface lipid and therefore differences in cleaning efficiencies that are cited (for different surfactants [20]) reflect differences in the amount of "internal hair lipid" removed. To support this conclusion, Shaw cites results from scanning electron micrographs (SEM) of hair washed with anionic surfactant (monoethanolamine lauryl sulfate) compared with SEM photographs of hair washed with the solvent ether (see Fig. 6.2). In addition, Shaw cites in vitro studies showing that various shampoos remove 99% of an artificial lipid mixture deposited on the hair.

Robbins [28] independently arrived at a similar "but not exactly the same conclusion" suggesting that shampoo surfactants in a normal two step shampoo operation are very effective in removing "surface" lipid deposits; but not as effective for removing free lipids that are bound within the interstices of 18-MEA on the surface. Furthermore, because of their limited penetration into hair, shampoos are not effective for removing much internal lipid. In addition, there are data to support the conclusion that free lipids are an integral part of the hair surface and should not be completely removed from the surface, see the section of Chap. 2 entitled, *Surface Lipids of Human Hair* including Table 2.15.

Table 6.11 offers some evidence for the effectiveness of current shampoos for removing a sebaceous-type soil from wool fabric in moderately soft water (80 ppm hardness). These data show that a cocomonoglyceride sulfate (CMGS) shampoo at only 5% concentration (5% shampoo and l% A.I.) under these laboratory conditions approaches the efficiency of boiling chloroform in a 4 h soxhlet extraction for removing lipid soil (Spangler synthetic sebum, see Chap. 2) from wool swatches. On the other hand, the soap containing shampoo of Table 6.11 is not very effective in removing this lipid from hair. The normal usage concentration of shampoos is 20–25%. The solution to hair ratio in normal shampoo usage is lower than in this experiment, however, this variable probably does not make a substantive difference. Wool swatches were used in this experiment instead of hair, because most shampoos are too effective to provide distinctions in removing sebum from hair under these conditions.

Another experiment involved comparing the total amount of extractable lipid from hair after washing with two different shampoos in a half-head test. These shampoos were selected because they displayed differences in their ability to remove sebum from hair in the laboratory. This experiment was performed twice, using five subjects per test. Both on-head tests show no significant difference in the amount of extractable hair lipid after shampooing the hair with these two shampoos (see Table 6.12). This result suggests that the laboratory test is more sensitive for detecting differences in sebum removal than the half-head test. It also suggests that both shampoos are removing most of the surface hair lipid deposits in the on-head procedure.

If large differences in cleaning efficiency really exist between most shampoos in consumer usage, then other variables such as lather or fragrance would not likely have a large impact on the consumer's assessment of cleaning efficiency. However, it is well known that variables such as fragrance or lather do have a large impact on the consumers' perception of cleaning efficiency by different shampoos, see Sect. 6.4. See the subsection 6.4.3.3.under Sect. 6.4. The above results are

Table 6.11 Shampoo versus chloroform extraction of wool fabric

% Shampoo	% Sebum removed[a]	
	CMGS formula	Soap ctg. formula
0.5	63	18
1.0	76	32
2.0	86	53
5.0	91	77

Test procedure: Wool swatches were soiled with synthetic sebum and weighed to determine the amount of soil deposited. The swatches were then washed in a tergitometer with CMGS and soap containing (dry hair) shampoos at varying concentrations. The swatches contained approximately 10% sebum. The temperature was 105–110°F, time was 30 s, and a 200/1 solution to wool ratio and 2–30 s water rinsings was used

[a]These percentage values were obtained by extracting these same wool swatches in boiling chloroform for 4 h in a soxhlet apparatus after shampooing and comparing the residue weight versus total soil deposited. So for practical purposes, boiling chloroform for 4 h provides 100% sebum removal

Table 6.12 Sebum on hair clippings and lipids after half-head shampooing with shampoos of different laboratory sebum removing potential

	Formula	% Sebum[a] removal in lab	Amount lipid[b] extracted using alcohol (4 h)
Test #1	TEALS liquid	54	3.0
	Tas-6-1065	82	3.0
Test #2	TEALS liquid	54	4.2
	Tas-6-1179-A	88	4.2

[a]Values obtained using synthetic sebum and 0.5% surfactant and the procedure described in Table 6.11

[b]*Test procedure*: Hair clippings were taken from both sides of heads after half-head shampooing (two applications of shampoo) on five subjects per test. Clippings were combined into two sets, keeping treatments separate. Each set was randomized, divided into three equal portions (~5.5 g each), and extracted in a Soxhlet apparatus for 4 h with ethanol. The lipid extract is expressed as a percentage of the dry weight of the hair for an average of triplicate determinations

consistent with the conclusion that current shampoos are very efficient for cleaning "surface" lipid deposits from the hair.

Statements contrary to the conclusions of Shaw and Robbins exist in the scientific literature. Schuster and Thody [29] state that "shampooing" with sodium lauryl sulfate is an ineffective means of removing hair lipid. Thompson et al. [21] report from in vitro testing that anionic surfactants remove polar components of sebum more readily than nonpolar components (paraffin waxes); the implication being that nonpolar components of sebum are not efficiently removed from hair by normal anionic shampoos. Clarke et al. [30] concluded that laureth-2 sulfate is one of the most effective surfactants for removing virtually all sebaceous components from hair. Lauryl sulfate is not as effective for removing fatty acids in the presence of water hardness. It is nevertheless, highly effective for removing other sebaceous components from hair. Shorter chain-length surfactants (less than C12) are, as expected, less effective for removing lipid components from hair.

The effect of temperature on the selective removal of sebum components from hair was also compared by Clarke et al. [31] for sodium laureth-2 sulfate and ammonium lauryl sulfate. Laureth sulfate was found to be the more effective detergent at both 21°C (70°F) and 43°C (110°F). Surfactant efficacy decreased with temperature providing a slightly greater selectivity in component removal at the higher temperature than at the lower temperature.

The ability of anionic surfactants to remove hair lipid is dependent on surfactant structure, concentration, agitation, temperature, time, and other variables including other soils on the hair. In addition, detergents like sodium lauryl sulfate do not penetrate rapidly into hair and should not be expected to remove the same amount of lipid from hair at the same rate as a penetrating lipid solvent like ethanol.

Under optimum conditions such as in vivo shampooing, anionic surfactants are nearly as effective as chloroform or ether (non-penetrating lipid solvents) for removing deposited surface lipid. In most of the tests described in the literature, care was taken to exclude conditioning products, containing cationics and cationic polymers or silicones, setting resins, and hard water to provide more control over

the experiments. Obviously these variables must be included before we can arrive at a full understanding and a consensus about the efficiency of anionic shampoos for cleaning hair lipids from the hair surface.

Other soils have not been studied so extensively. However, Robbins et al. [32] have shown that C12 alkyl sulfates or alkyl ether sulfates, the traditional shampoo surfactants, do not remove cationic surfactants from hair as effectively as shorter chain length surfactants. Shorter chain length anionics such as deceth-2 sulfate is more effective for removing cationics than lauryl or laureth sulfates. In addition, alkyl ether sulfates are more effective for removing fatty acid soils in the presence of water hardness than alkyl sulfates [32]. These results support the rationale for using mixed surfactant systems for the most effective way to remove a mixture of hair soils.

6.3.4.6 Surface Versus Internal Lipid

Human hair contains both surface lipid and internal lipid, and these lipids are incorporated into lipid layers and bound to the hair or surface deposits as summarized in Chap. 2. 18-MEA is the primary lipid on the hair fiber surface, and it is covalently bound to underlying proteins through thioester linkages [33]. However, there is generally an appreciable amount of free lipid (not covalently bound) in the surface (Chap. 2). Thus, there will be more free lipid in the surface, closer to the roots than the tips, and there will be more free lipid the longer the time interval between shampooing and with less hair damage. Support for these conclusion stems from defining the hair surface as the top 3–5 nm and using X-ray photoelectron spectroscopy to measure the amount of free lipid in this surface via C/N analyses. Details are described in Chap. 2.

Some of the internal lipid is structural material and part of this structural lipid in the cuticle layers is covalently bound, while some is non-covalently bound by weaker attractive forces (free lipid). Covalently bound lipids cannot be removed chemically by shampoos or lipid solvents, but abrasive actions of shampoos can break and thus remove large particles of the hair surface containing structural lipids. But, part of the non-covalently bound lipids can be removed by shampoos. Supporting this conclusion is the increasing evidence that structural lipid, probably part of the beta layers of the cell membrane complex, can be removed over time by shampooing [34, 35], see Chap. 1. Furthermore, some cationic-anionic interactions illustrate cell membrane complex damage. These and analogous interactions likely lead to loss of inert Beta layer material. This effect is described in more detail later in this chapter.

When the hair has not been shampooed for several days, the total amount of lipid extractable from “oily” hair by a hair swelling solvent like ethanol can be as high as 9% of the weight of the hair (Jacob, private communication). A sizable fraction of the “total” hair lipid is not removed by shampooing or by extraction with a non-penetrating, low-boiling lipid solvent like ether. We have obtained as high as 4.2% ethanol extractable matter from hair cut from heads immediately after shampooing

two times with a triethanol ammonium lauryl sulfate (TEALS) shampoo (Jacob, private communication) (see Table 6.12).

Curry and Golding [36] concluded that the rate of extraction of lipid from hair by solvents is very slow. Even after 100 Soxhlet cycles with ether (four successive extractions), a significant amount of lipid can be obtained by additional extraction. As indicated before, Shaw [20], using SEM techniques, suggested that washing hair with either ether or shampoos in a one-step application removes virtually the entire surface "free" lipid from hair and that differences in cleaning efficiencies of surfactants relate to the amounts of internal hair lipid removed. Recent XPS data shows that shampooing does remove some free lipid from the surface of hair, but even after shampooing, an appreciable amount of free lipid remains in the surface layers and it is likely bound in the interstices of 18-MEA, see Chap. 2. Shaw found that one-step shampooing removes approximately 50% of the ether extractable matter.

Koch et al. [9] reported that repeat shampooing removes 70–90% of the ether-extactable lipid, and that enzymatic hydrolysis of hair after ether extraction, followed by extraction of the residual membranes yields "internal lipid." Koch found the composition of this internal lipid to be somewhat similar to that of surface hair lipid, see Chaps. 1 and 2. Koch therefore concluded that internal lipid of hair must in part originate from the sebaceous glands (see the section entitled Cell Membrane Complex of Chap. 1).

See Chap. 2 for a description of the techniques used to extract covalently bound lipids and free lipids and internal and external lipid from the hair. Koch suggested that external lipid may be extracted by boiling ether saturated with water followed by ethereal hydrochloric acid. The former solvent removes neutral surface lipid; the latter solvent removes calcium-bridged fatty acids attached to the hair surface. He suggested that surface lipid so defined is removed under conditions that simulate the "strongest shampooing conditions imaginable."

This definition of surface lipid by Koch probably provides a high estimate for surface hair lipid. Another definition is the amount of lipid removed by a double application of an anionic surfactant. This latter definition probably provides a more realistic estimate for the practical "removable" surface hair lipid. However, if one accepts this latter definition, then the amount of lipid left in hair after shampooing represents internal lipid and may be estimated by solvent extraction (ethanol) after shampooing.

Capablanca and Watt [37] examined wool fiber that had been washed with detergent and extracted with various solvents using a streaming potential method to estimate the effect of free lipid (non-covalently bound) on the isoelectric point of wool fiber. These scientists found that the surfactant washed wool (containing the most free lipid) provided an isoelectric point of 3.3 while the most effective lipid solvent extracted hair provided an isoelectric point of 4.5. These data show that the true isoelectric point of the surface hair proteins is close to 4.5 and that free lipid which contains fatty acids is an important and essential component of the surface of animal hairs. So, the more free lipid present in these surface layers, the lower the isoelectric point of the keratin fibers. Therefore, all of the free lipid is not totally

Table 6.13 Amount of hair lipid in oily versus dry hair after shampooing

	Average amount of lipid recovered	
	Weight (g)	% Weight of hair
Dry hair	0.164	3.6
Oily hair	0.161	3.6

removed from the surface layers by shampooing and this lipid is important to the isoelectric point and to the adsorption of ingredients onto human hair and to other important surface properties of hair.

Table 6.13 summarizes data from an experiment conducted to determine if the quantity of internal hair lipid differs in dry (chemically unaltered hair) versus oily (chemically unaltered) hair. Immediately after shampooing two times with a TEALS shampoo, hair clippings were taken from three oily-haired panelists and three dry-haired panelists and extracted with boiling ethanol. The results suggested similar quantities of internal hair lipid in these six hair samples.

Test Procedure: Six panelists were selected for this test, three having dry hair and three oily hair, as judged by both beauticians and the panelists themselves. Hair clippings were taken from heads after shampooing with a TEALS shampoo, using the usual two-step application procedure. The clippings were combined from all three dry-hair and all three oily-hair panelists. They were randomized into three replicates (sets) per sample, and Soxhlet extracted in triplicate for 4 h with ethanol.

This test result suggests that the amount of internal lipid in dry and oily hair is virtually identical. Therefore, the primary differences between dry and oily hair lipid are in the amount and the composition of the surface lipids. In summary, the current literature suggests that human hair contains lipid at or near its surface and that it also contains internal lipid. The surface lipid provides many of the negative physical characteristics attributed to oily (greasy) hair, while some of the interior lipid will slowly diffuse to the surface upon successive washings (shampooing) or extractions. Furthermore, this internal hair lipid is similar (but not exactly the same) in composition to the external hair lipid. Hair also contains bound or structural internal lipid that is presumably resistant to shampooing. Further details on the composition of hair lipid are described in Chaps. 1 and 2.

6.3.4.7 The Transport of Hair Lipid

After shampooing, the Free Lipid content of the surface layers of hair has been considerably reduced, but it is still at a significant level. As time passes from shampooing, sebum (produced by the sebaceous glands) and epidermal lipid (produced by the cells of the horny layer of the scalp) are transferred to the hair because of its greater surface area and absorptive capacity. Creeping of sebum along the hair has been suggested by Gloor [38], although Eberhardt [39] concluded that creeping does not occur along single hair fibers. Eberhardt suggests that transport occurs

primarily by mechanical means such as by contact of hair with scalp (pillows and hats), rubbing (combing and brushing), and hair-on-hair contact.

Distribution of sebum along the fibers by combing and brushing is very important, and wicking as occurs in textile assemblies is most likely also involved [40, 41]. The net result is that the rate of accumulation of lipid is fastest for oily hair and after the lipid accumulates, beyond a given level, it interferes with the appearance and overall aesthetics of the hair causing fibers to clump or to adhere together, producing the appearance of limp hair.

The composition of the lipid soil itself may influence its transport, because ingredients that either lowers the surface tension of the sebum or increases its fluid nature (makes it less viscous) can facilitate transport and even increase the perception of oiliness. In addition, other ingredients left behind on the hair surface such as conditioning agents, may exacerbate oiliness in an analogous manner.

Hair characteristics such as fineness, degree of curvature, and length are also relevant to the transport of lipid and to the influence of lipid on hair assembly properties. For example, fine, straight hair will provide optimum characteristics for transport of sebum. This type of hair will also provide the maximum amount of hair clumping by a given amount of lipid, thus it will appear oilier and more limp than curly hair. For example, curly-coarse hair will tend to inhibit transport and also to minimize the influence of tress clumping and compacting. Among all hair properties, increasing fiber curvature provides the greatest influence against the cohesive forces of hair lipid and the resultant compacting (limpness) of fibers in assemblies such as tresses [42].

6.3.4.8 Cationic Soils

Dye staining tests [43] on wool fabric or hair swatches (containing cationic) and ESCA studies on hair containing mono-functional cationic surfactant [25] show that a single washing of hair with an anionic detergent does not remove all of the quaternary ammonium compound from hair. Radiotracer studies of cotton fabric containing presorbed sodium lauryl sulfate (SLS) by Hsing et al. [44] indicated that SLS sorbs to the fabric in an equimolar quantity to the deposited quaternary ammonium compound. Robbins et al. [45] found that by presorbing anionic surfactant (SLS) to hair and then treating it with cationic (dodecyltrimonium bromide), the presorbed anionic enhanced the adsorption of the cationic to the hair. These results suggest that mono-functional cationics are resistant to removal by anionic surfactant because they form adsorption complexes on hair and these have the potential to build up on hair.

Robbins et al. [32] determined that washing mono-functional cationic surfactants like cetrimonium chloride from hair treated with a conditioner using normal alkyl sulfates or alcohol ether sulfates does not remove all of the cationic from the hair. In addition, the anionic detergent can build up with the cationic. However this type of build up generally levels after five to six treatments. Shorter chain length surfactants like deceth-2 or -3 ether sulfate do not build up in the same manner. In addition, hair

matting has been reported in vivo and attributed by Dawber and Calnan [46] to the adsorption of cetrimonium bromide on hair.

Certain cationic polymers have also been reported to build up on hair [8]. Even low-charge-density cationic polymers like polymer JR have been reported to be resistant to removal from hair surfaces by anionic surfactant [47, 48]. For example, in one study 3% sodium lauryl sulfate, after 1 min, removed 50% of the polymer JR from the hair and nearly 70% in 30 min. However, some strongly bound cationic polymer was still attached to the hair and resistant to removal by anionic surfactant after 30 min.

Hannah et al. [48] showed that polymer JR deposits on hair in the presence of excess sodium lauryl sulfate. This deposited complex is highly substantive to hair and resists removal by either water or 3% sodium lauryl sulfate. Therefore, adsorption complexes of polymeric cations also resist shampooing from hair.

Polyethyleneimine, a high charge density cationic polymer, is even more strongly bound to hair than polymer JR, and has been shown to be resistant to removal by anionic surfactant [49]. For example, PEI-600 was sorbed onto hair and tested for desorption toward a 10% shampoo system. After 30 min, less than 20% of the PEI was removed and only about 30% PEI was removed after 6 h. For additional details on the adsorption and removal of cationic polymers from hair, see Chap. 8 and the references therein.

Lipid soils or deposits are more readily removed from hair surfaces by normal shampooing. However, the foregoing results clearly show that cationic soils are resistant to removal by anionic surfactant, and it appears that anionic surfactants are not capable of completely removing high-charge-density cationic polymers from hair.

6.3.4.9 Other Soils

The original hair spray lacquers of the 1950s were more difficult to remove from hair than the anionic and neutral polymers of today's hair-setting products. However, no systematic study of the ease or difficulty in removing these ingredients from hair could be found in the scientific literature. Gloor [50] examined the influence of hair spray on re-oiling; however, no systematic study of the effects of hair spray on the ease of removal of hair lipid has been reported.

Calcium-bridged fatty acid may be deposited onto hair even in shampoos containing anionic surfactant such as ammonium lauryl sulfate. In addition, calcium has been shown by Smart et al. [51] to concentrate in the cuticle and the medulla and at much higher levels in oxidized hair versus chemically untreated hair. It is also well known that acid rinses may be used to remove calcium-bridged fatty acid from hair, and anionic sulfate surfactants appear to remove some fatty acid deposits from hair. However, divalent copper (cupric ion) adsorbs to hair and is reported to be resistant to removal by anionic surfactant [10].

Published literature regarding the efficacy of anionic surfactant systems for removing particulate soils such as soot, hydrocarbons, etc. could not be found.

As indicated earlier, as particle size decreases below about 1 μm, the resistance to removal should increase and the particles will become increasingly difficult to remove. Particles below 0.1 μm will be very difficult to remove [18].

6.3.4.10 Rate of Re-Oiling of Hair

Breuer [52] described the kinetics for re-oiling of hair in terms of sebum production and sebum removal. He derived the following expression to describe the rate of re-oiling:

$$m = A/K\left(1 - e^{-Kt}\right)$$

where m = amount of sebum on the hair (at any time after cleaning), t = time after cleaning (min), A = production rate of sebum (12.5×10^5 ng/min), and K = rate constant for sebum removal.

Using experimental data, the above expression was solved numerically by Breuer suggesting that in a 4 day period; approximately 65% of the sebum that is produced is lost from the head by rubbing against objects such as pillows, combs or brushes. Breuer concluded that shampoo and post-shampoo treatments influence the re-oiling rate of hair. As indicated earlier, anionic surfactants alone do not stimulate the rate of re-fatting [20], although antidandruff agents have been shown to affect sebum production. For example, selenium sulfide has been reported to increase the rate of sebum production [19, 53], zinc pyrithione [19] and climbasole, two other antidandruff agents have also been shown to behave similarly by increasing hair greasiness [19]. Ketoconazole on the other hand has been shown to decrease the rate of sebum production [53].

6.4 Perceptions in Cleaning Hair and Subjective Testing of Shampoos

With the advent of 2 in 1 shampoos, a new era was begun in cosmetic science. Differences in the performance between 2 in 1 conditioning shampoos can be relatively large. These effects can be detected in laboratory tests, in half head tests, and even in consumer tests on cell sizes smaller than N = 100. To the cosmetic scientist, this is a positive situation. We could now turn our attention to real product performance for conditioning shampoos and work to create products that are really better, not only in the laboratory, but products that consumers will see as better. This situation was created by a combination of new technology and consumers becoming willing to accept different standards of performance for shampoos. I believe this same situation exists for other opportunities in hair care in the future, e.g., hair body or hair thickening shampoos.

The situation is not as clear for cleaning shampoos. However, with the new soils that we are leaving behind on hair for superior conditioning, body and style control, perhaps new performance opportunities in hair cleaning will also become feasible in the future. Nevertheless, the following discussion is useful for all product types when the differences between real product performances become relatively small, a situation that could occur for 2 in 1 shampoos or high performance conditioning shampoos in the twenty-first century.

Questions regarding the removal of sebaceous soil and other soils from hair are fundamental to the action of shampoos; however, another fundamental question is: Which is more important to the sale of shampoos—the actual abilities of different shampoos to remove soil from hair, or factors relating to the perception of cleaning such as lather, viscosity, fragrance, etc.? Laboratory or in vitro tests are critical to provide an understanding of shampoo behavior. However, subjective tests are ultimately involved to evaluate the consumer's response to the total product. The next section describes some of the more common subjective tests used in shampoo development and raises some important questions.

6.4.1 Shampoo Performance

The evaluation of overall shampoo performance is determined by the hair effects that the product provides and by the properties of the shampoo itself (properties that do not directly influence hair effects, but are important to the consumer). A helpful distinction defines hair effects as all performance attributes of the shampoo evaluated after rinsing, and shampoo properties as all performance attributes noted or evaluated prior to and during the rinse step.

6.4.2 Hair Effects and Discernibility Versus Perception

For this discussion, discernibility is considered as the objective (not necessarily numerical) ability of the users of a product to isolate and to discriminate between effects on hair without being influenced by related stimuli such as fragrance, lather, viscosity, etc. Perception on the other hand is the subjective response to a hair property, and this response is influenced by all related stimuli including the hair property itself, advertising and label copy, and all related shampoo properties.

The question of whether or not a hair effect is discernible to a given percentage of consumers is relevant to the understanding of the perception of a product and to understanding why a product does or does not sell well. However, its answer will often be in doubt. This is because it is difficult for consumers or panelists to be objective and to isolate and measure performance properties without being influenced by other product properties. For pragmatic (financial) reasons, insufficient blind tests are generally conducted to determine discernibility, because the

bottom line is sales not objective understanding. It is for this reason that many executives question the relevance of testing performance in isolation. Thus, judgment is involved to answer questions of discernibility and subjectivism often interferes in its evaluation and interpretation.

6.4.3 Different Tests to Evaluate Shampoo Performance

Some of this author's conclusions relevant to different types of shampoo (product) tests are described below. In general, objective discernibility of a hair effect becomes progressively less important as one proceeds from laboratory to sales tests. This is because subjective perceptions involving psychologically related stimuli become more important as one moves from the laboratory (where experimental control isolates discernibility from perception) to sales testing.

6.4.3.1 Laboratory Tests

Certain laboratory tests (tress combing, fiber friction, light scattering, sebum removing ability, etc.) can be more sensitive than consumer's evaluations (see Sect. 6.3.4.3 and Chap. 9). However, the most severe constraint with laboratory testing is that laboratory measurements are often only a portion of the related consumer assessment. For example, fiber friction is only a small part of how the hair feels to a consumer or how easily her or his hair combs and hair combing is only a portion of hair conditioning to consumers.

6.4.3.2 Half-Head Tests with Evaluations by Trained Cosmetologists

These tests are side-by-side comparisons and can be more precise than most assessments by consumers (who rely on memory comparisons) for discerning most important hair effects. It can also be argued that half-head tests generally involve short-term effects, and they may be misleading with regard to long-term effects.

6.4.3.3 Blind Product Tests

The standard 2-week crossover blind product test with a large panel size ($N \sim 300$) is a relatively sensitive means for discerning whether or not product differences exist between different shampoos. On the other hand, long-term effects due to buildup or product interactions may be either not detected or further complicated by the 2-week crossover design. One further difficulty, even in short-term evaluations, is in understanding the meaning of the differences detected in this type of test procedure. It is

very easy to take the conservative stance and to rule out a product if it loses in a blind product test. Yet, I often wonder how many excellent products never got to the marketplace because of an inconsequential loss in a blind product test.

The overall data of a blind product test are usually more consistent and more sensitive than the majority of the individual panelists (see Table 6.14). This table summarizes data from a blind test in which a baby shampoo was compared with a high-foaming TEALS based shampoo containing the fragrance and color of the baby shampoo. This test was actually two tests run back to back, comparing these two products for four 2-week intervals. Among the 73 panelists, for all attributes other than lather and fragrance, fewer than 14 panelists were consistent in their ratings. The consistency obtained in overall preference and in all hair effect attributes was not beyond that expected by random chance. These results show that differences do exist between these two shampoos, but only about one-third of this panel could repeat their lather and fragrance choices between these two products. Less than 15% of this panel could distinguish between any hair effect differences between these two products, that is could duplicate their choice for any hair effect.

There is a significant lather preference but not a significant fragrance preference. Only a small percentage of the panelists were capable of duplicating their choice for hair effects; e.g., for flyaway and luster 9 and 8 panelists were able to duplicate their choice. However, the overall test results suggest a difference for flyaway and luster ($p = 0.02$ and 0.04 respectively).

Only a small percentage of these panelists appear to be capable of discerning hair effect differences between these two products. Nevertheless, the statistics for the overall test results suggest a difference for example in flyaway and luster

Table 6.14 Adult shampoo versus baby shampoo (blind, back to back tests)

Specific attribute	Probability Test 1 (N = 75)	Probability Test 2 (N = 73)	Total consistent	Ratings of 73
Overall preference	0.85	0.66	16	
Lather	0.99	0.88	23	
Ease of rinsing	0.62	0.99	11	
Cleaning efficiency	0.88	0.95	13	
Feel of wet hair	0.50	0.88	12	
Ease of combing (wet)	0.44	0.77	11	
Feel of dry hair	0.72	0.99	10	
Ease of combing (dry)	0.44	0.44	10	
Flyaway	0.89	0.83	9	
Luster	0.77	0.84	8	
Fragrance	0.55	0.62	23	
Softness	0.72	0.74	10	

Note: This experiment suggests that most of the users individually do not clearly discriminate between these two shampoos, although the test results overall clearly show differences. The repeat scores for overall preference are not beyond that expected by random chance. The overall probability that the TEALS product is preferred is at $p = 0.05$

(overall $p = 0.02$ and 0.04 respectively), but only 9 and 8 of these panelists were able to duplicate their choices. These results lead one to question whether large or meaningful differences exist between hair effects of this baby shampoo and adult shampoo. In light of the consistency ratings, one questions how discerning consumers (panelists) as individuals really are to shampoo performance attributes.

Blind tests with larger groups have been run comparing a related TEALS shampoo formulation versus this same baby shampoo, where the sebum-removing capabilities of these two products in laboratory tests were equivalent. Once again, an attempt was made to match the color and fragrance of these two products. The TEALS product was clearly superior in various laboratory foam tests and in foam property evaluations in half-head testing. The panelists as a group significantly preferred the TEALS product for cleaning efficiency, foaming properties, and for overall performance as well as for several hair effect attributes. Apparently, the superior foaming character of the TEALS system provided a "halo" effect that subconsciously reflected in the cleaning efficiency evaluation and in several of the hair effect attribute evaluations.

6.4.3.4 Identified Product Tests

Discernibility is very difficult to interpret from Identified Product Tests, because perceptions from label copy, fragrance, lather, and other stimuli often influence or even overwhelm true performance differences. Several years ago, we tested a protein-containing shampoo, both blind and identified, 3 months after its national introduction. The blind test scores showed that in spite of color, form, and fragrance variables, panelists could not discern between the hair effects of that protein shampoo and the hair effects of another leading competitive brand. However, panelists exposed to concepts, label copy, and product names in an identified test provided highly significant wins for this same protein-containing shampoo in hair effect scores, against their favorite brands. These panelists ($N \sim 300$) in a projectable identified consumer test were so taken in by the concept and label copy of the protein-containing shampoo that they simply repeated the concept and label copy in their performance ratings. This suggests that in some instances, in identified consumer tests, particularly in the event of a popular concept, the true performance attributes of shampoo products may be ignored and even overwhelmed by the impact of the concept.

6.4.3.5 Sales Tests

Performance properties in sales tests are even more subject to the influence of psychologically related stimuli than any other type of test. However, since a sales test is long-term, longer-term performance benefits or negatives will have some bearing on the test outcome. Thus, a sales test can provide some index of longer-term performance, particularly if an effort is made to control other variables.

Unfortunately, this is difficult to do, and the cost of a sales test is considerably greater than for an identified consumer test.

The conclusions from the above descriptions of different tests suggest that cleaning shampoos are more successful in the marketplace for concept and for advertising execution than for real differences in hair effect benefits. This same situation does not exist for 2 in 1 shampoos. This conclusion suggests that the true cleaning differences provided by shampoos that are currently in the market place may indeed be real. However, they are relatively small and subtle or the sale of these products would not be so influenced by psychologically related stimuli and advertising. On the other hand, the current differences between conditioning offered by conditioning shampoos are relatively large. When subtle hair effect differences are complemented by quality advertising execution and other psychological stimuli (sensory effects) an opportunity for a marketplace success exists. Thus, when larger hair effect differences are created an even greater opportunity exists in the marketplace particularly when the hair effect differences are complemented by good advertising execution. When larger hair effect differences are provided, then the need for psychological reinforcement or sensory effects is not as great as in the former situation when only subtle hair effect differences between competing products are provided.

6.5 Shampoo Foam or Lather

The foaming potential of shampoos does not directly influence the physical behavior of hair fibers. However, as indicated in the previous section, shampoo foam can influence the consumer's perception of hair characteristics including cleaning. Therefore, a brief introduction into this important shampoo property is provided in this section.

A useful work leading to the present understanding of shampoo lather has been described by Neu [54] and by Hart and colleagues [55, 56]. Neu pointed out that the traditional Ross-Miles [57] shampoo lather evaluation using an active concentration of about 0.1–0.2% is unrealistic for simulation of shampoos. He suggested lather testing at an order of magnitude greater in active surfactant concentration. Neu used a kitchen food mixer to generate shampoo lather in the laboratory. The high shear rates of a food blender produce lather from surfactants that is more similar to that obtained on hair under actual shampooing conditions than provided by cylinder shake test methods such as in Ross-Miles.

Hart and DeGeorge [55] used a Waring blender similar to Neu to generate shampoo lather and measured drainage rates of the lather to provide an index of lather viscosity. Hart and DeGeorge [55] distinguished between foam and lather for shampoo evaluation. These authors pointed out that "foam" is a broad generic term consisting of "any mass of gas bubbles in a liquid film matrix," whereas lather is a special type of foam formed during shampooing and other processes and "consists of small bubbles that are densely packed," thus resisting flow. Hart's drainage test

has been shown by Domingo Campos and Druguet Tantina [58] to produce results that relate to actual in-use salon testing.

Some useful conclusions from Hart's work are as follows: A synthetic sebum load generally lowers lather quality. This is consistent with the well-known observation that the second shampoo application lathers better than the first shampoo application because less sebaceous soil is encountered in the second application. Hart also demonstrated that traditionally known "foam booster" additives such as lauramid DEA or cocamido propyl betaine should more correctly be called lather modifiers (amides do modify lather feel and tend to make a thicker, creamier lather). However, these additives generally do not increase the amount of lather; they tend to suppress shampoo lather.

Foams or lathers are formed when air is introduced beneath a liquid surface and it expands to enclose the air with a film of liquid. The film must be elastic to produce a foam or lather and it must retard the loss of air from mechanical shock and from soils. Materials that provide low surface tensions provide greater foam volumes and higher foam stability. Longer chain length materials also provide more foam stability. Polymers and other additives improve foam and lather stability by increasing intermolecular cohesive forces within the film. Fatty alkanolamides and betaines improve foam stabilization by increasing the film elasticity. Alkanolamides pack between anionic surfactant molecules forming an aggregate film and thus reduce the anionic surfactant head group repulsion. This effect allows a larger more cohesive aggregate film to form around the air, giving rise to improved lather properties.

Hart and Neu provided a useful beginning to a better understanding of shampoo lather, of lather testing, and of the effects of additives on shampoo lather. However, Hart's lather drainage rates are only one of the important components of shampoo lather that is relevant to the consumer's perception. Lather feel and the rate of lather generation are two other important components of shampoo lather. As of this writing, methods for these important lather components have not been described in the scientific literature.

6.6 Sorption or Binding of Ionic Ingredients to Hair

The sorption of shampoos and conditioners to hair is essentially a reaction at or near the hair fiber surface. Therefore, the approach adopted in this section is to present the latest information on the nature of the hair fiber surface and to provide a summary of the latest hypothesis on the adsorption of ingredients (surfactants and hair conditioners) to hair. Then, a synopsis is provided of the interactions of ionic ingredients of shampoos, conditioners, and ionic dyes with hair. Since ionic dyes are sometimes used in sorption studies as model systems for surfactant molecules, some material on the sorption of ionic dyes has been included in this Sect. 6.6.1.

6.6.1 *Binding to the Hair Fiber Surface*

The virgin hair fiber surface is covered with a thin (about 1–3 nm) covalently bound lipid layer of 18-MEA that is attached by thioester linkages to a proteinaceous cell membrane called epicuticle [33]. Jones and Rivett [59] described that Sims and XPS "indicate the surface of virgin wool fibers is almost exclusively hydrocarbon". Swift [60] provided evidence that the proteinaceous membrane beneath the 18-MEA is about 13 nm thick [60] (see Fig. 6.4). In Fig. 6.4, the epicuticle is described as two layers of protein consisting of KAP-5 and KAP-10 proteins [61] and it is bonded to the A-layer on its interior and to 18-MEA on its exterior.

XPS estimates by Ward et al. [62] suggest that 18-MEA is 1.0 ± 0.5 nm thick and molecular modeling shows it to be 1.08 nm [63]. However Ward's estimate was made on hair containing virtually no free lipid in the surface of the fibers and the modeling was with no free lipid in the 18-MEA layer. Evidence from XPS, described in Chap. 2 in the section entitled *Surface Lipids of Human Hair*, suggests that free lipids are bound within the 18-MEA layer. But, when free lipids are removed by shampooing the chains of 18-MEA fold back on themselves as suggested by Zahn et al. [64] decreasing the thickness of the surface lipid layer, see Chap. 1 in the section entitled, *Thickness of the Cuticle Beta Layers* for an explanation of the thickness of the Beta layers which also applies to the surface lipid layer.

As hair is exposed to repeated washing, drying and rubbing actions and to sunlight, changes occur at and in these surface layers removing some free lipids by shampoos and removing 18-MEA by photochemical attack on thioester.

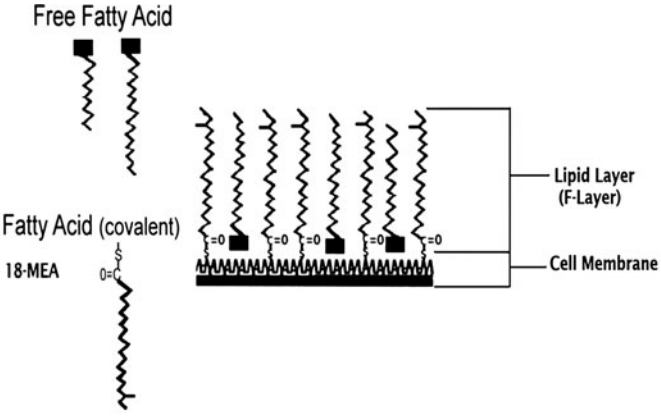


Fig. 6.4 Schematic illustrating the hair fiber surface with 18-MEA and free lipid on the external layer with epicuticle proteins on the second and third layers

Furthermore, disulfide and other bonds are oxidized by sunlight and small fractures are formed between layers of the surface from bending, stretching and abrasive actions. These actions remove some 18-MEA and proteins exposing new protein material which is gradually oxidized forming sulfur acids, such as sulfonate and with a decrease in the covalently bound and free lipids the virgin hair surface is converted from a hydrophobic entity with little surface charge to a hydrophilic, polar and negatively charged surface. The more exposure of the hair to chemical and abrasive actions, e.g., the further from the root ends the more hydrophilic, more polar and more negatively charged the surface becomes. See Chap. 4 in the *Summary of chemical changes to hair by permanent waving* and Chap. 5 in the *Summary of bleaching hair proteins* and the *Summary of sunlight oxidation of hair proteins* sections.

6.6.2 *Overview of the Binding of Shampoos and Conditioners to Hair*

The major ingredient in most shampoos is anionic surfactant. Although other surfactants (amphoteric or nonionic), thickening agents, lather modifiers, conditioning agents, colors, and fragrance—are also normally present. Most shampoos are formulated near neutrality and are based on the anionic surfactant salts of lauryl sulfate or laureth sulfate (most commonly up to 3 moles of ethoxylation), see Sect. 6.2.3.1.

Creme rinses, on the other hand, are basically compositions containing cationic surfactant in combination with long-chain fatty alcohol or other lipid components. For additional details on product compositions, see Sect. 6.2.5.3 and consult references [65], Flick's formulations [66], product ingredient labels, and the books by Hunting [4, 5].

The attachment of ingredients to hair fibers is fundamental to the action of conditioning agents. The amount of sorption or uptake of an ingredient by hair from an aqueous solution is governed by its attraction or binding interactions to the keratin, versus its hydrophilicity or binding interactions to the aqueous phase, and the rate of diffusion of the ingredient into the hair.

For conditioning ingredients in shampoos and hair conditioners, Robbins et al. [67] suggested that adsorption is more critical than absorption because the conditioning ingredients are relatively large species and low temperatures are employed in contrast to wool dyeing where diffusion is critical. Furthermore, they proposed a hypothesis considering adsorption to hair in terms of a continuum between a charge driven adsorption process and a hydrophobically driven process see Fig. 6.5. An example of what is essentially a purely charge driven process is the adsorption of a water-soluble cationic surfactant like dodecyltrimonium chloride from an aqueous solution onto hair above the isoelectric point of hair. This adsorption process is

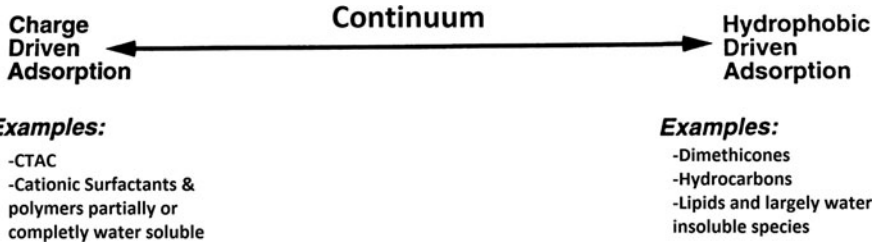


Fig. 6.5 Schematic illustrating the hypothesis [67] of a continuum between a charge driven and a hydrophobically driven mechanism for adsorption of conditioning agents to keratin surfaces

driven by the attraction of the positively charged quaternary ammonium ion to the negatively charged hair fiber surface.

At the other end of the spectrum, is the adsorption of a water insoluble dimethicone onto hair from an anionic shampoo medium. This adsorption is driven by the fact that wet hair comes into contact with a medium where insoluble silicone or another hydrophobic species is suspended in the aqueous phase. The additional water from the wet hair and from rinsing perturbs the system, and adsorption occurs primarily because of entropy; that is to keep the silicone suspended requires additional molecular organization that can only be overcome by putting additional energy into the system. Thus, the silicone comes out of suspension and some of it attaches to the water insoluble hair. Although the primary driving force for this hydrophobic adsorption process is entropy or the decrease in the organized orientation of molecules in the system, hydrophobic binding to the hair fiber surface is also involved.

This mechanism was presented as a continuum rather than as just two extremely different processes. The continuum exists because as we change the structures of the adsorbing species, or the hair or the solvent medium, we can see the mechanism moving toward a more charge driven or a more hydrophobically driven process. For example, in current hair conditioners, as we change the quaternary ammonium species from a short chain to a longer chain species, e.g., from cetyl to stearyl or to bihenyl, or as we move from monoalkyl quats to dialkyl quats, these structural changes cause the charge driven process to take on more hydrophobic character. On the other hand, if we take a water insoluble dimethicone and add polarity by adding amino groups, we decrease the amount of adsorption. However the adsorption that takes place, takes on some charge driven character if the aminosilicone is in a nonionic or a cationic surfactant medium as opposed to an anionic medium wherein complexes of low solubility are formed.

The binding interactions to keratin are influenced by the charge of the ingredient, its molecular size, and the isoelectric point of hair determined by its oxidation state (condition) and the amount of free lipid in the surface, the pH of the surrounding medium, other salts or components in the formulation, and ingredients that are attached to the fiber surface. The attraction to the aqueous phase is governed primarily by the hydrophilic including the charge character or the hydrophobic

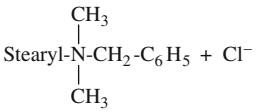
nature of the adsorbing ingredients. This property is determined by the ratio of nonpolar to polar substituent groups. If we are considering absorption, then we must consider diffusion rates that are governed primarily by molecular size, condition of the hair, pH and reaction temperature.

Since the isoelectric point of lightly damaged hair (the most common type) is so low, approximately 3.67 [68], its surface bears a net negative charge near neutral pH, where most shampoos are formulated. Although anionic surfactants bind to this hair surface (probably by their hydrophobic tails), the number of adsorption sites is comparatively small, relative to sites for cationic ingredients. Lauryl and laureth sulfate salts and salts of olefin sulfonate are also moderately hydrophilic. They appear to rinse well (but not completely) from hair, and therefore serve as good cleaning agents.

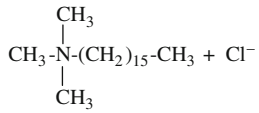
More anionic surfactant does bind to hair with decreasing pH, suggesting that low-pH shampoo formulations (below the isoelectric point) will leave more anionic surfactant behind after shampooing than neutral pH shampoos.

The diffusion of anionic surfactants into hair is also very slow, and it takes days for an average-size surfactant to completely penetrate cosmetically unaltered hair. Although some penetration of surfactant can and does occur, the major interactions of the surfactants of shampoos and creme rinses occur at or near the fiber surface; that is near the first few microns or more likely the first few nanometers of the hair surface.

One objective of high cleaning shampoos is to minimize sorption and/or deposition of its ingredients. On the other hand, the effects caused by conditioning shampoos and creme rinses are primarily due to the adsorption of ingredients at or near the fiber surface. Soaps and surfactants, lipids, cationic ingredients, and even polymers or polymer association complexes (see Chap. 8) have been used as conditioning ingredients in shampoos and/or conditioning products. Soaps deposit their hydrophobic salts on the hair or bind by metal bridging. Cationic surfactants and polymers attach substantively to hair by ionic bonds enhanced by Van der Waals attractive forces. The substantivity of most polymer association complexes is probably due to their hydrophobic nature, enhanced by Van der Waals forces and by entropy and possibly ionic bonds. Creme rinses are analogous to conditioning shampoos in causing hair effects chiefly by the adsorption of ingredients to hair. The primary active ingredient of most crème rinses is a cationic surfactant such as stearalkonium chloride or cetrimonium chloride.



Stearalkonium chloride



Cetrimonium chloride

More cationic than anionic surfactant binds to the hair surface above its isoelectric point and cationic surfactants are difficult to remove by rinsing. As a result, cationic surfactants are said to be substantive to hair. Similar to anionic surfactants,

diffusion of cationic surfactants into hair is slow. The more important interactions occur at or near the fiber surface (first few microns and more likely the first few nanometers of the fiber periphery), thus accounting for the low surface friction and the ability of creme rinse conditioners to make hair comb easier (see *Hair Fiber Friction* in Chap. 9). Most modern creme rinses contain a high concentration of a fatty alcohol such as cetyl-stearyl alcohol or a similar fatty material in addition to a cationic surfactant. Dye binding studies show that these alcohols bind to hair along with the cationic ingredient (absorption maximum shifts), resulting in easier combing and more effective conditioning than by the cationic surfactant alone.

The hair surface of unaltered or bleached hair is negatively charged at neutral pH. Thus, the positive end of the cationic surfactant has a greater affinity for the hair than for the hydrophobic alcohol, especially in bleached hair. Therefore, the cationic surfactant most likely serves as a bridge to bind the hydrophobic alcohol to the charged hair surface. A related bridging can be used to bind other hydrophobic ingredients such as dimethicones to bleached hair or to undamaged tip ends (more polar hair surfaces). The skillful use of bridging agents and formula stabilization are the keys to improved shampoo technology in the future, see the section on silicone polymers in Chap. 8.

The condition of the hair also affects the uptake and the diffusion of creme rinse and shampoo ingredients. A rule of thumb is that diffusion is faster into altered or damaged hair than into unaltered hair. Bleaching (oxidation; see Chap. 5) also lowers both the isoelectric and the isoionic points of hair, thereby attracting more cationic surfactant to the hair. Thus, the use of bridging agents is even more important to the adsorption to bleached hair than to chemically unaltered hair. Although diffusion occurs more readily into cosmetically altered hair, the more important hair effects are produced by conditioner and conditioning shampoo ingredients that bind at or near the fiber surface. Only in the case of severely damaged tip ends might internal binding be more important, and even here the distinction may be essentially semantic.

6.6.3 Transcellular and Intercellular Diffusion

Theoretically two pathways exist for diffusion into human hair [69] (see Fig. 6.6): (1) transcellular diffusion, and (2) intercellular diffusion. The transcellular route involves diffusion across cuticle cells through both high and low cross-linked proteins. On the other hand, intercellular diffusion involves penetration between cuticle cells and through the endocuticle and the cell membrane complex protein structures that are low in cystine content (low cross-link density regions). Gummer [70] and others separated intercellular diffusion into diffusion involving entry through either the cell membrane complex of the cuticle versus entry via the endocuticle and other non-keratinous regions of the fiber and then diffusion throughout the cortex via both the intercellular cement of the individual cortical

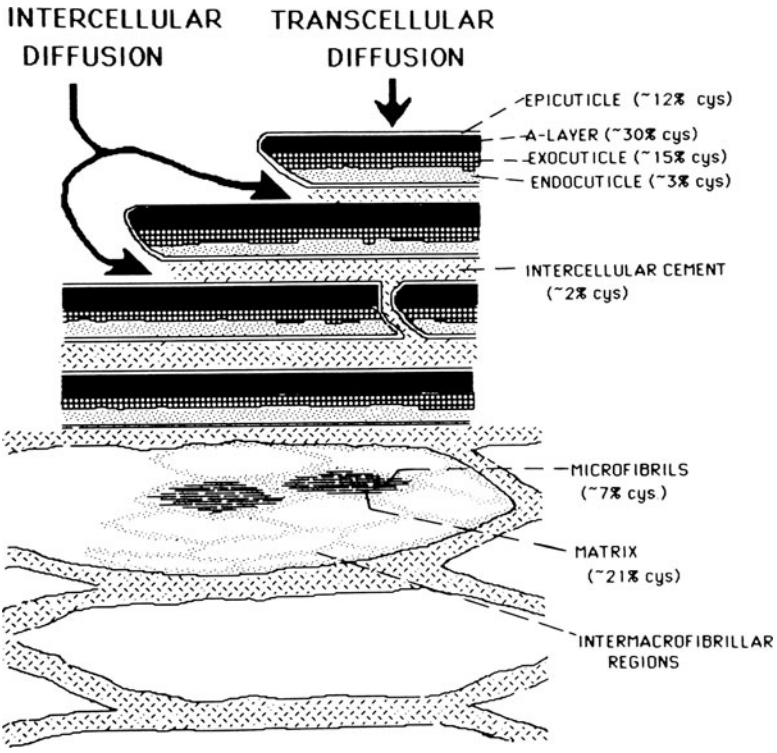


Fig. 6.6 Schematic illustrating transcellular versus intercellular diffusion. Note: the different histological regions are not drawn to scale

cells. The schematic of Fig. 6.7 illustrates the interconnecting pathways for intercellular diffusion through the non-keratin regions of hair.

More than seven decades ago, transcellular diffusion was the generally accepted route because of the much greater amount of surface area available for this type of penetration. However today, intercellular diffusion or diffusion through the non-keratin regions of the intercellular cement and the endocuticle, see Fig. 6.7 has become widely recognized as a route for entry of molecules (especially large ones such as surfactants or even species as small as sulfite near neutral pH).

Hall [71] as far back as 1937 first proposed intercellular diffusion between the scales of wool. Such diffusion has been demonstrated by Leeder et al. [72] for metal complex dyes. Leeder demonstrated that a large cationic dye (rhodamine B, 479 Da); triphenyl pyrazine, a neutral molecule (311 Da); and the high molecular weight anionic oligomeric Synthappret BAP (>3,000 Da) all penetrate hair through the intercellular route.

Both diffusion routes probably can occur under the right circumstances considering the right sized molecule, the right solvent system and the degree of damage to the hair. The intercellular route is probably preferred in many instances particularly

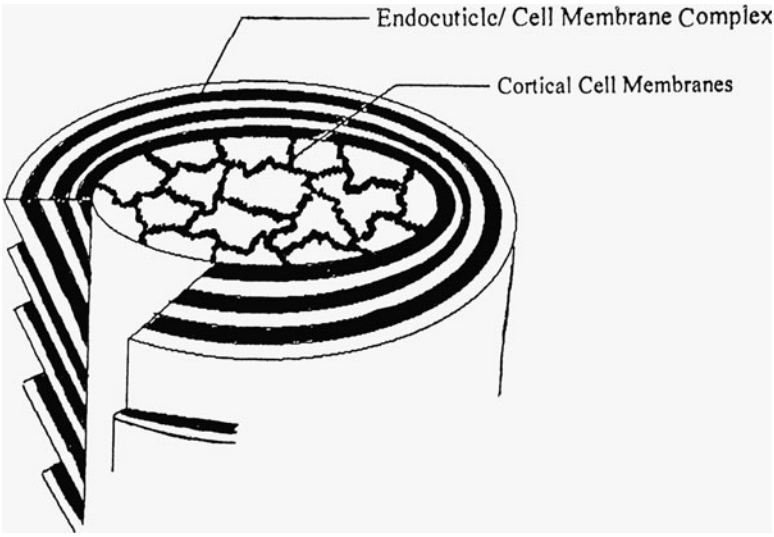


Fig. 6.7 Schematic illustrating the non-keratinous route for diffusion into hair

for large molecules because the low-sulfur, non-keratin proteins are more easily swollen than the highly cross-linked regions (see Chap. 1). However this distinction does not exclude some penetration via the transcellular route. For small molecules, transcellular diffusion under certain conditions might be the preferred route, but not the exclusive route, especially if the highly crosslinked exocuticle is damaged or cross links are broken by reducing or oxidizing treatments. The preferred view today is essentially that hair is viewed as consisting of a number of domains of differing chemistry and accessibility, rather than as uninterrupted pathways from the hair surface to the core of the fiber.

For large metal complex dyes (>650 Da), Leeder et al. [72] demonstrated that intercellular diffusion of these materials occurs into wool fiber. Certain alcohols such as butanols, are considered non-swelling solvents and have been shown by Jurdana and Leaver [73] not to penetrate into the cortex of wool, but to penetrate readily into the cortex of human hair via the intercellular regions.

For many dyeing processes and the penetration of large organic molecules into animal hairs, initially the surfactant, the dye or organic material penetrates primarily but not exclusively into the fibers through the cell membrane complex and the endocuticle and intermacrofibrillar regions. Then during the later stages of reaction, more of these molecules migrate into the more highly cross-linked exocuticle and A-layer of the cuticle cells and the matrix of the cortex.

Cosmetics companies have promoted the concept of penetration as positive. To this end, it can be shown that penetration of large molecules into the cortex occurs when fibers are split or cracked, see Figs. 6.8, 6.9 and 6.10. Figure 6.8 depicts a split hair in cross section surrounded by non split hairs. All fibers were treated with a cationic conditioner followed by staining with Red 80 dye prior to cross-sectioning.

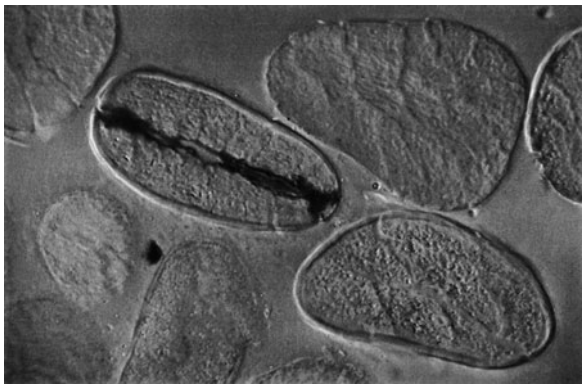


Fig. 6.8 Penetration of a cationic surfactant into a split hair. The split hair was treated with conditioner cross-sectioned and then stained with red 80 dye

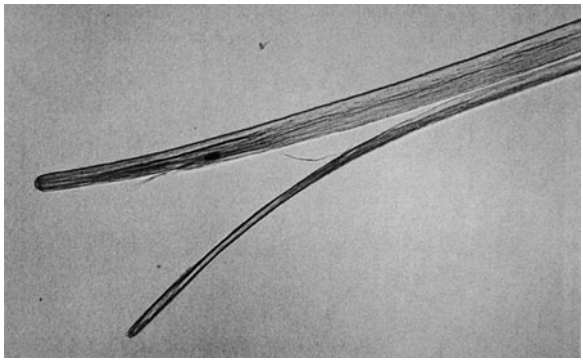


Fig. 6.9 Light micrograph of a split hair stained with red 80 dye after shampooing with sodium lauryl sulfate. Dye does not stain the hair with anionic adsorbed

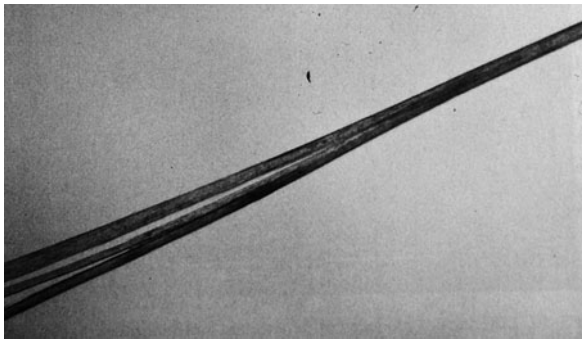


Fig. 6.10 Light micrograph of a split hair treated with a cationic conditioner and then stained with red 80 dye. Note staining on all surfaces including the split surface (where the cationic conditioner adsorbs). Compare to Fig. 6.9

Note the large amount of stain at the split. Figure 6.9 depicts a split hair fiber treated with cationic conditioner and not stained. Contrast this to Fig. 6.10 depicting a split hair fiber treated with cationic conditioner and stained. Note the staining occurs on all surfaces even the interior surfaces of the split.

On the one hand, penetration may be beneficial if the penetrant is an adhesive or a plasticizing material. However, penetration into the intercellular regions of hair,

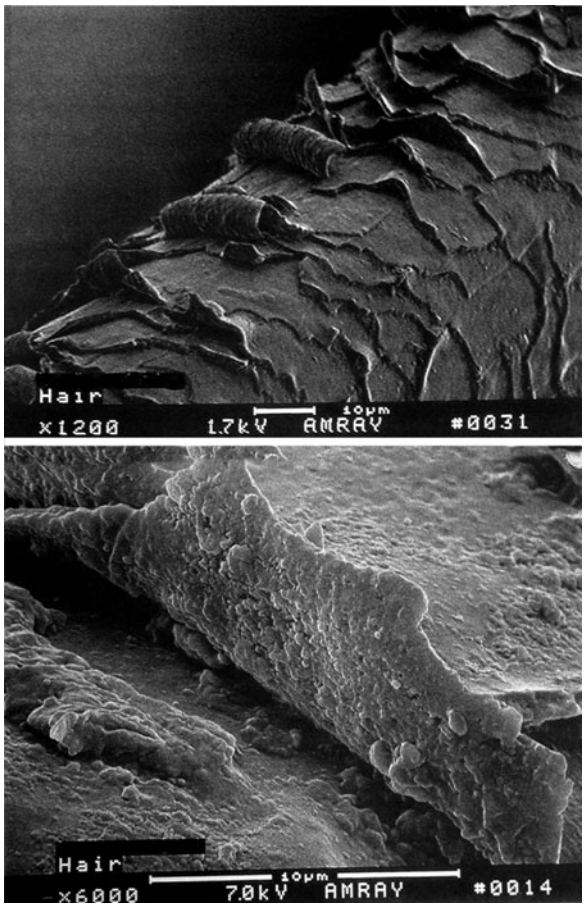


Fig. 6.11 Lifted scales from penetration and deposition underneath the scales. The treatment was alternating treatments of specific conditioner and shampoo ingredients

between the scales, could also degrade the non-keratin components [34, 35] and even cause scale lifting, a form of hair damage, see Fig. 6.11. This phenomenon will be described in more detail later in this chapter.

6.7 Sorption Theory

6.7.1 Equilibria and Kinetics of Ionic Surfactant and Dye Interactions with Keratin Fibers

There are two thermodynamic quantities of pragmatic significance that characterize hair-surfactant interactions: the chemical potential (μ), and the heat of reaction (H).

6.7.2 The Chemical Potential (Affinity)

The chemical potential describes the tendency of solute, surfactant, or dye to move from solution to the fiber. It is analogous to a partition coefficient. Gibbs suggested the use of this parameter in place of the free energy for systems where the free energy has the disadvantage of depending on the amount of the system [74].

In actual practice, the change in the standard chemical potential ($\Delta\mu^\circ$) is evaluated as the measure of the tendency of the solute to move from the solution to the fiber that is the "relative affinity" of the substance for the fiber relative to the solution phase. This parameter is generally called the affinity and is usually expressed as ion affinities instead of as molecular affinities (see Table 6.15). One expression that describes the standard chemical potential, if the ion forms ideal solutions, is:

$$-\Delta\mu^\circ = RT \ln(D)_f/(D)_s$$

where R = gas constant (1.987 cal/degree mole), T = absolute temperature (O°C = 273.16°K), $(D)_f$ = concentration of ion in the fiber, and $(D)_s$ = concentration of ion in solution. This equation suggests that the affinity of an ingredient for hair in an aqueous system is governed by the ratio of its binding attractions to the fiber and its hydrophilicity (the binding attractions to the aqueous phase). Perhaps the most commonly used expression for determining this parameter is the one that determines the affinities of free dye acids. When the fiber is half saturated with acid (about 0.4 mmoles acid per gram for wool or hair), the following expression applies:

$$-\Delta\mu^\circ = 4.6\,RT\ \text{pH midpoint}$$

Therefore, anion affinities may be calculated from the pH of the midpoint of the titration curve for keratin fibers and acids (see Table 6.15). For a more

Table 6.15 Molecular weight and anion affinities of acidic ingredients[a]

Acid	Molecular weight	pH midpoint	Total affinity μ° (kcal)	Anion affinity[b] (kcal)
Hydrochloric	36.5	2.32 (0°C)	5.8	0.5
Ethyl sulfuric	126	2.33 (0°C)	5.8	0.5
Isoamyl sulfonic	152	2.58 (0°C)	6.4	1.1
Benzene sulfonic	158	2.63 (0°C)	6.6	1.3
Octyl sulfuric	210	3.47 (25°C)	9.1	3.8
Dodecyl sulfonic	250	4.02 (25°C)	11.1	5.8
Dodecyl sulfuric	266	4.08 (25°C)	11.0	5.7
Orange II	328	4.63 (25°C)	12.6	7.3

[a]Calculated from the pH midpoint titration data of Steinhardt et al. [75]
[b]Calculated assuming the hydrogen ion affinity to be 5.3 kcal [76]

comprehensive treatment of this subject, including appropriate expressions for different experimental conditions, see Chap. 4 of the book by Vickerstaff [74], the paper by Lemin and Vickerstaff [77], and the paper by Han et al. [78].

The data of Table 6.15 show that anion affinities increase with increasing molecular weight or molecular dimensions. The same has been shown for cations. Ion affinities are generally independent of pH, and largely consist of the sum of the bond strength of the ionic attachment and Van der Waals attractive forces, which can be very powerful in large molecules (see Chap. 8). Furthermore, as Van der Waals attractions increase, the hydrophobicity of the surfactant increases, further increasing the affinity of the molecule for keratin in an aqueous system.

6.7.3 Heat of Reaction

The heat of reaction of a surfactant or dye with a fiber is the other thermodynamic property that has practical significance. It describes the effect of temperature on equilibrium that is whether more or less of an ingredient combines with the fibers at equilibrium as the temperature changes. For cosmetics, the heat of reaction is not nearly as important as the chemical potential, since the change in the standard heat of reaction (ΔH°) with temperature over the narrow range of temperatures used in personal care products is comparatively small. The simplest procedure to determine ΔH° involves adsorbing a quantity of surfactant onto hair and then determining the amount of surfactant that is removed at different temperatures. A plot of the logarithm of the concentration of desorbed surfactant (in solution) at equilibrium versus 1/temperature provides a straight line with slope of ΔH° [79]. Other methods for determining this parameter have been described by Vickerstaff [80] and others.

6.7.4 Oxidative Theories of Dyeing

Two primary models have been presented to account for the uptake of electrolyte by keratin fibers [80–83]. Both models consider hair as an ion exchange resin with positive and negative groups. The Gilbert-Rideal theory assumes that all ions are adsorbed by attachment to specific sites in the keratin—namely, the ionized carboxyl and amino groups. On the other hand, the Donnan membrane theory assumes the existence of an imaginary membrane between two phases, the solution and the fiber. The existence of a Donnan potential between the two phases then determines the partitioning of the ions between the fiber and the surrounding solution.

Both models appear to quantitatively explain the phenomenon of dyeing keratin fibers with ionic dyes, although, there has been considerable controversy between supporters of each theory [80, 84, 85]. Oloffson [86, 87] in a critical analysis of these two theories concludes that the Gilbert-Rideal theory provides the better fit to experimental data.

The objective here is to acquaint the reader with these two theories, to provide reference material if more information is desired [80–83] and to point out that most of the subsequent discussion considers interactions with specific sites in the fiber.

6.7.5 *Kinetics of Ionic Reactions with Keratin Fibers*

Summary of Reaction Steps:

Reactions of hair fibers with solute in solution may be considered as a multi-step process involving:

1. Diffusion through solution;
2. Adsorption or interaction at the fiber surface;
3. Diffusion or transport into the fibers; and
4. Reaction at internal sites in the fibers.

Whenever diffusion through solution is rate determining, reactant concentrations are generally low (about 0.1% or less), the rate is dependent on agitation, and the reaction is usually characterized by low activation energies (3–5 kcal/degree mole).

Adsorption at the "exposed" fiber surface is generally rapid for ionic ingredients, and the surface becomes filled (with respect to solute) during the first few minutes of reaction. Diffusion into the fibers is generally the rate-determining step for most hair fiber reactions and is usually characterized by higher activation energies (10–30 kcal/degree mole).

Ionic reactions are generally rapid and therefore not rate-determining. However, reactions that involve breaking and formation of covalent bonds are sometimes slower than diffusion into the fibers and therefore can be rate-determining. One example is the reduction of the disulfide bond by mercaptans at acidic pH.

The amount of an ingredient that penetrates into the fibers and the extent of penetration are governed by the following factors:

Reaction temperature
Molecular size
Cross-link density of the fibers
Fiber swelling
Reaction time

The rate of diffusion or penetration generally increases with increasing temperature and fiber swelling, whereas it decreases with increasing cross-link density and molecular size of the penetrating species. Obviously, the extent of penetration increases with time.

Liquid water at room temperature can penetrate across the entire fiber in less than 15 min, and in less than 5 min at 92°F [88], whereas more than 6 h is required for single fibers to equilibrate in a humid atmosphere, and even longer for a fiber assembly. Dyes like methylene blue (molecular weight ~320) and orange II (molecular weight ~350) generally require over an hour to penetrate through all

the cuticle layers to the cortex. Similar penetration times would be expected for typical anionic and cationic surfactants used in shampoos and hair conditioners.

6.7.6 Diffusion Coefficients and Diffusion into Keratin Fibers

See Sect. 6.6.3. Williams and Cady [89] suggested that diffusion processes may be considered as three types: free or molecular diffusion; forced diffusion; and obstructed diffusion. Free or molecular diffusion applies to the transport of matter by random thermal motion. Forced diffusion involves transport by forces other than random molecular motion, for example, pressure gradients within a fluid or electrical or magnetic fields.

Diffusion coefficients involving only free diffusion are called true or intrinsic diffusion coefficients; processes involving both free and forced diffusion are called mutual diffusion processes. Experimentally, one cannot usually evaluate free diffusion in kinetic studies on keratin fibers. Therefore, the usual practice is to apply equations derived from Fick's laws for free diffusion to data involving mutual diffusion. This practice provides apparent or approximate diffusion coefficients, instead of intrinsic diffusion coefficients, and compromises the fundamental significance or interpretations of these processes involving molecular motion such as the activation energies or entropies of activation.

In the remaining part of this book, no attempt is made to distinguish between free and mutual diffusion: the term "diffusion" is used loosely. For more comprehensive treatment of intrinsic and mutual diffusion, see the books by Crank [90] and Alexander et al. [91] and the review by Williams and Cody [89].

6.7.6.1 Fick's Laws of Diffusion

Fick's first law for unidirectional diffusion states that J, the flux (flow), is proportional to the gradient of concentration (dc/dx) [92].

$$J = -D(dc/dx)$$

This equation states that the flow of a substance through a surface perpendicular to its direction of movement is directly proportional to the rate that its concentration changes with distance, (dc/dx), the concentration gradient. The proportionality constant D is the diffusion coefficient and has the dimensions of area per unit time usually expressed as cm^2/s.

Fick's second law for unidirectional diffusion may be derived from his first law [93], and it provides the fundamental differential equation for diffusion of an isotropic medium (similar properties in all directions):

$$\frac{\delta C}{\delta t} = D\frac{\delta^2 C}{\delta X^2}$$

Most kinetic studies of diffusion into keratin fibers employ equations derived from this form of Fick's law and provide approximate diffusion coefficients, assumed to be constant throughout the diffusion reaction. However, Crank [94] has provided equations for evaluating diffusion data under a wide variety of circumstances, including a variable diffusion coefficient described later in this chapter.

6.7.6.2 Experimental Approaches for Diffusion Study

The simplest experimental approach for fiber diffusion study involves periodic analysis of the decreasing concentration of solute in solution surrounding the fibers (a limited volume of solution). A second approach provides a constant concentration of solute, "infinite bath," and requires direct analysis of solute in the fibers. Crank and Hill and others have developed diffusion equations for both experimental situations and some of these are described below.

6.7.6.3 Diffusion into a Cylinder from a Solution of Limited Volume

Crank [95] described several equations for diffusion into a cylinder with changing solute concentration and a constant diffusion coefficient (D). One of these equations describes diffusion from a stirred solution of limited volume into a cylinder of infinite length (see below). where Q_t = amount of solute sorbed in time (t), Q_∞ = maximum sorption capacity of solute by hair, and r = fiber radius.

$$\frac{Q_t}{Q_\infty} = 2\left|\frac{2}{\sqrt{\pi}} \quad \left|\frac{Dt}{r^2}\right|\right|^{\frac{1}{2}} \quad \text{-} \cdots \cdots$$

If a plot of Q_t/Q_∞ versus the square root of time is linear, then the latter terms of this equation (not depicted) may be neglected, and the expression above applies. The approximate diffusion coefficient may then be calculated from the slope of the plot with knowledge of the fiber radius. Weigmann [96] determined that this equation describes the reaction of dithiothreitol with wool fiber. A similar expression has been derived by Hill for diffusion into a semi-infinite solid, as shown below [97].

$$Q_t/Q_\infty = 2\,A\,\sqrt{Dt/\Pi}$$

Hill defined a semi-infinite solid as a tissue of irregular shape where no exact mathematical treatment is possible. Alexander and Hudson demonstrated that this expression applies to the diffusion of orange II dye into wool fabric [98]. A plot of

Q_t/Q_∞ versus the square root of time should be linear with a slope of $2A \sqrt{D/\prod}$. The A term represents the total surface area of the fibers used in the experiment. The variation of fiber surface area with diameter is described in Chap. 9.

6.7.6.4 Diffusion into a Cylinder from an "Infinite Bath"

Vickerstaff [80] noted that equations describing diffusion into an infinite cylinder (e.g., hair) or into a plane slab (e.g., skin) from a constant solute concentration (infinite bath), assuming a constant diffusion coefficient, are of the following general form:

$$\frac{Q_t}{Q_\infty} = 1 - A\, e^{-BK} - C\, e^{-FK} - G\, e^{-HK} \ldots .$$

A, B, C, F, G and H are known constants; $K = Dt/r^2$ for the case of the infinite cylinder; and r equals the fiber radius [99]. In this instance, to determine the diffusion coefficient, simply carry out a sorption experiment to a fixed time (t) at a given temperature and agitation rate, and determine the amount of surfactant or dye sorbed by the fibers (Q_t). The value of Q_t/Q_∞ is calculated, and from the appropriate graph (Fig. 6.12) the corresponding value of $K = Dt/r^2$ is determined. Since t, r, and K are all known, D may be calculated from $D = Kr^2/t$. Obviously,

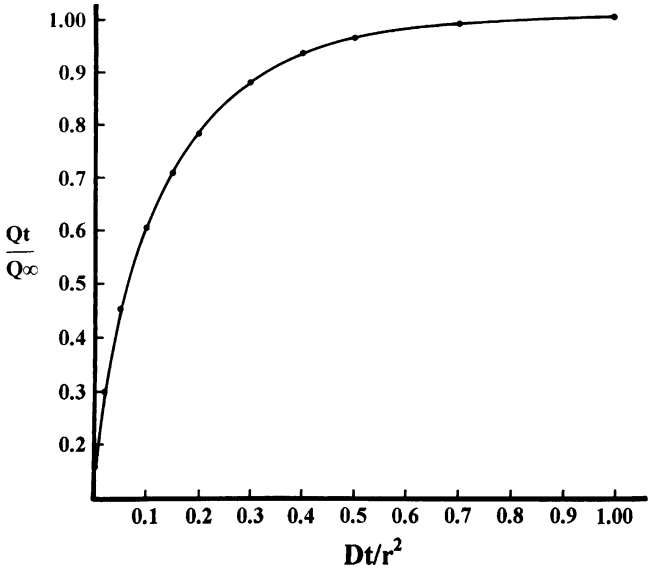


Fig. 6.12 Diffusion into a cylinder from an infinite bath. A plot from data by Vickerstaff. For lower proportions of penetration (See the data and plots by Vickerstaff [99])

replication of the experiment and determination of an average value for D provides a more reliable estimate. Davis and Taylor [100] used this procedure for the determination of diffusion coefficients for orange II dye into nylon fiber, and Holmes [101] used a modification of this procedure for evaluating diffusion coefficients for diffusion of dyes into human hair.

6.7.6.5 The Case of a Variable Diffusion Coefficient

The diffusion equations described in the previous section have been derived from Fick's second law for unidirectional diffusion with the assumption that the diffusion coefficient is constant throughout the reaction. Crank [94] also derived equations for evaluating diffusion data for systems with a variable diffusion coefficient that can be used to test one's data.

King [102, 103] found that the transport of either water or alcohol through keratin fibers is examples of reactions with a variable diffusion coefficient. For the wool-water vapor system [102] at 25°C, the diffusion coefficient is approximately 10^{-9} cm^2/s as the fiber approaches dryness. However, at high regains, it is of the order of 10^{-7} cm^2/s. Theoretically, the diffusion coefficient for this system could approach the limiting value of 2.27×10^{-5} cm^2/s, the diffusion coefficient for water in water [104]. The variable diffusion coefficient in this case is caused by changes in internal fiber structure, during the reaction that involves increasing water binding with increasing regain and portions of the fibers becoming more "water like" with increasing regains.

In general, the penetration of solvents (that promote swelling) into polymers may be described as processes with a variable diffusion coefficient. For more comprehensive treatment of this subject, see the books by Alexander et al. [105] and Crank [93–95].

6.7.6.6 The Influence of Temperature on the Diffusion into Keratin Fibers

The activation energy (E_{ACT}) describes the effects of temperature on reaction rates. For example, the rate of a reaction with a higher E_{ACT} will respond more readily to temperature changes than one with a lower E_{ACT}. The activation energy can also help to distinguish between diffusion through solution and diffusion through the fibers, for example, an E_{ACT} of 3–5 kcal/degree mole generally indicates that diffusion through solution is rate-limiting, whereas an E_{ACT} of 10–30 kcal/degree mole generally indicates that diffusion through the fibers is rate-limiting.

The E_{ACT} is an important parameter in the collision theory of reaction rates. It approximates the energy of activation in the transition state theory of reaction rates [106]. As indicated, diffusion reactions for keratin fibers generally involve mutual diffusion coefficients, because they involve transport components other than temperature. The theoretical interpretations in terms of molecular motions that

follow assume no complications from electrical gradients and other factors of forced and obstructed diffusion that may be involved in these interactions and therefore the following discussion should be interpreted with caution.

According to the collision theory of reaction rates, the effect of temperature on the rate of a chemical reaction is defined by the Arrhenius equation:

$$K = A\, e^{-E_{ACT}/RT}$$

where K = the specific reaction rate, A = the pre-exponential function (entropy related term), R = the gas constant (1.987 cal/degree mole), and T = the absolute temperature (0°C = 273.16°K).

The following two equations have been derived from the Arrhenius equation and are convenient for determining the E_{ACT} experimentally.

$$\log\ K = \frac{-E_{ACT}}{2.303\ RT} + \log\ A$$

$$E_{ACT} = \frac{RT_2T_1}{T_2 - T_1} 2.303\ \log \frac{K_2}{K_1}$$

The first equation shows that the E_{ACT} may be determined by plotting the logarithm of reaction rates against 1/T and multiplying the slope by −2.303 R. The second equation shows that the E_{ACT} may be evaluated by determining the rates of reaction at two different temperatures and calculating this parameter from the corresponding expression above.

The E_{ACT} for diffusion of water into wool fiber decreases with increasing water content, from 7.5 Kcal/degree mole at lower regains to about 4.8 kcal/degree mole at 16% water content [102]. The E_{ACT} at higher regains is essentially the same as for the diffusion of simple solute molecules (sulfonate dyes) in water [107]. This suggests a two-phase system at higher regains, with water molecules diffusing through the aqueous phase within the fibers [102].

Activation energies for diffusion of the simple dye orange II into both human hair and wool fiber have been reported. Gilbert [108] has shown that the rate of diffusion of orange II into keratin fibers obeys the Arrhenius equation between 0 and 80°C. He also reported activation energies of 28 and 23 kcal/degree mole for diffusion of orange II into human hair and wool fiber, respectively. Robbins determined similar activation energies (at low pH) for the diffusion of this same dyestuff into human hair and merino wool (29 and 24 kcal/degree mole, respectively). The higher activation energy for diffusion into human hair is probably related to its higher cross-link density.

In addition, Robbins and Scott [109] found that the E_{ACT} for diffusion of orange II into merino wool is pH dependent, decreasing from 24 to 11 kcal/degree mole with increasing pH from 1 to 7. Robbins and Fernee [110], while studying the swelling of stratum corneum by anionic surfactant as a function of pH, suggested that ionic bonding dominates the reaction between hair and anionic surfactant at pH 1,

whereas hydrophobic bonding between surfactant and hair is more important near neutral pH. Therefore, if this reaction between ionic surfactants or dyes, and hair is predominately ionic in character at acidic pH, then the reaction near neutral pH involves a greater amount of hydrophobic character and the activation energy should show a corresponding change, as found.

The temperature-independent term of the Arrhenius equation (A, or the pre-exponential function) is generally considered to be analogous to the entropy of activation of transition state theory [92]. Robbins found that this parameter varies from 10^4 to 10^{-1} cm^2/s for the diffusion of orange II into merino wool at pH 1 and pH 6.7 respectively. Hudson [111] reported a value of 10^{-2} for this parameter at unspecified pH. Assuming the analogy of the pre-exponential function and the entropy of activation hold for this mutual diffusion process; then the diffusion of anionic dye or surfactant into keratin fibers requires entropy of activation that increases with decreasing pH. This effect suggests that there is less precise orientation in the activated state at low pH than at neutral pH for the diffusion of anionic dye or surfactant into keratins. Thus, the reaction of anionic surfactant with keratin that is dominated by hydrophobic bonding (near neutral pH) requires a higher degree of molecular orientation than the ionic reaction at acidic pH. This assumption is entirely reasonable for a hydrophobically driven process compared with a charge driven process.

6.7.6.7 Molecular Size and the Concept of Pore Size

Speakman [112, 113] theorized that keratin fibers consist of a solid containing holes or pores. Although the cell membrane complex is not actually holes, with some imagination, one can visualize this region of entry into the fibers as not too far removed from Speakman's proposal. This concept suggests that the rate of diffusion into a fiber containing holes depends on the effective molecular radius of the diffusing species and on the size and frequency of holes in the solid. Apparently the size of the holes will depend on the swelling medium and reaction conditions employed.

Assuming this theory to be valid, Holmes [101] investigated the size of these holes in human hair via a dye diffusion study in 0.1 N hydrochloric acid, and suggested the holes are approximately 15 Å in diameter. Wilmsmann [114], on the other hand, attempted to determine the relationship between molecular size of cationic dyes and their penetration into human hair by microscopic observation of fiber cross-sections that were previously dyed. Although his reaction conditions were limited (30 min at 36°C in strong alkali), Wilmsmann observed that none of the larger species of triphenyl methane dyes penetrated into the cortex, whereas the smaller aromatic diamines did. He concluded that there is a hindrance to the penetration of larger molecules. The largest diamine that Wilmsmann examined, 4-amino diphenylamine has a corresponding molecular diameter of 6–8 Å which he concluded is near the critical molecular diameter for penetration.

The apparent discrepancy between the conclusions of Holmes and Wilmsmann probably stems from Wilmsmann's use of a qualitative analysis for short reaction times and Holmes use of a quantitative analysis for longer reaction times. Also, different hair and different experimental conditions were involved. However, Wilmsmann's results do provide a feel for the reaction times and size requirements for the penetration of cationic ingredients through the cuticle. In addition, Holmes data suggests that any ingredient that is approximately spherical or larger in all dimensions than 15 Å may experience a slow rate of penetration into hair at low pH.

6.7.6.8 Cross-Link Density and Diffusion Rate

Table 6.16 describes the influence of cross-link density in different keratin fibers on diffusion rate. These data show that the rate of diffusion into keratin fibers decreases with increasing cystine content and therefore with increasing cross-link density. One may conclude that reactions that decrease the cross-link density of hair (e.g., bleaching) will lead to hair that is more rapidly penetrated, and its penetrability will increase with increased bleaching. Decreasing cross-link density obviously increases the rate of transcellular diffusion.

6.8 The Binding of Ionic Groups to Hair

The interactions of ionic ingredients such as acids, alkalis, and neutral salts with keratin fibers are of major importance to shampoos, creme rinses, ionic conditioners, and the group of hair dyes referred to as rinses. In this section, these interactions are described as:

Hydrogen ion interactions;
Hydroxide ion interactions; and
Interactions of salts near neutrality with keratin fibers.

This section considers the hypothesis that ionic interactions with hair may be partly represented (at low or high pH) as hydrogen ion or hydroxide ion interactions

Table 6.16 Cross-link density and diffusion rates

Type of keratin fiber	% Cystine calculated from % sulfur	Relative diffusion [115] coefficient at 60°C using orange II dye
Human hair	14.0	1.0
80's merino wool	11.3	1.9
6's mohair	9.2	3.4
56's down wool	8.8	5.0

[a]Calculated from % sulfur, assuming all sulfur exists as cystinyl residues, and a residue weight of 178 Da

with hair, even though most of us are concerned with the combination of surfactants or dyes with hair. This approach becomes more palatable when one considers that for every hydrogen ion or hydroxide ion that interacts with hair, an accompanying anion or cation must also interact to maintain electrical neutrality. The counterion that combines with the fibers is determined by its affinity for the hair and its concentration relative to competing counterions. Hydrogen ion interactions are most important when only simple inorganic cations (e.g., sodium or potassium) are present. These ions have a low affinity for hair relative to hydrogen ion and therefore compete most effectively for sites on hair at higher pH values which is at low hydrogen ion concentrations.

The acid or hydrogen ion combinations are described in this manner: The combination of simple acids (hydrochloric and ethyl sulfuric) with hair; the influence of anions on the combination of hydrogen ions with hair; and the combination of low molecular weight organic acids with hair. Hydroxide ion interactions are essentially a mirror image of the hydrogen ion interactions and are described in three analogous sections. However, interactions of salts near neutrality are governed by mechanisms of interaction near pH 7 that are somewhat different from those of low and high pH.

6.8.1 Hydrogen Ion Interactions with Keratin Fibers

6.8.1.1 The Maximum Acid-Combining Capacity

The maximum acid-combining capacity of keratin fibers, from reaction with simple acids such as hydrochloric, phosphoric, or ethyl sulfuric acids, is approximately 0.75 mmole/g for unaltered human hair and about 0.82 mmole/g for wool fiber [116–120]. This value approximates the number of dibasic amino acid residues in the fibers [117] that is the combined amounts of arginine, lysine, and histidine (see Table 6.17). The primary sites for interaction with acid (protons) are probably the carboxylate groups of aspartic and glutamic acids (ionized by

Table 6.17 Data on the acid combining capacity of unaltered hair and wool[a]

	From 0.1 N HCl	Orange II combined from formic acid	Orange II combined from 0.1 N HCl	Arginine + lysine + histidine
Human hair	0.77 0.82 [113] 0.87–0.91 [121]	0.67–0.77 [119]	[b]	0.81 [118]
Wool fiber	0.8–0.9 [122, 123]	0.81 [119] 0.83 [117]	0.82–0.85 [124] 0.96	0.88 [118]

[a]Data expressed as mmole/g dry hair
[b]Because of competing hydrolysis, etc., reliable values for equilibrium could not be obtained

interaction with the dibasic amino acid residues) and the dibasic amino acid groups themselves.

This acid–base reaction involves protonation of a basic site on/in the fiber forming a positive charge on the fiber that attracts a negative ion to it. Steinhardt et al. [116] determined that the uptake of chloride ion by wool corresponds to the uptake of hydrogen ions during reaction with hydrochloric acid. Robbins has shown the same effect to be true for human hair.

Maclaren [117] took advantage of this counterion effect and developed a test for the acid-combining capacity of keratin fibers by measuring the uptake of the anion of orange II dye (p-hydroxy-1-naphthyl azobenzenesulfonic acid) from formic acid solution. Robbins et al. [119] used this test to study the variation in the acid-combining capacity of hair among individuals. In that study different persons who had treated their hair with different cosmetic treatments and have exposed their hair to different environmental conditions were examined.

6.8.1.2 Variation in the Acid-Combining Capacity of Unaltered Hair

Hair samples were collected from 20 female Caucasians ages 10–30 who had never bleached, dyed, or permanent-waved their hair. These hair samples were analyzed by Maclaren's method for the acid combining capacity. The average uptake was 0.70 mmole/g. Analysis of variance indicated significant differences among these hair samples beyond the alpha = 0.01 level.

6.8.1.3 Variation in the Acid Combining Capacity of Altered Hair

Bleaching decreases the acid-combining capacity of both human hair [119, 121] and wool fiber [124]. Analysis of hair samples bleached to different extents shows that the acid-combining capacity decreases with increased bleaching [119] (see Table 6.18). Amino acid analysis of these same hair samples shows no change in the basic amino acid residues. Therefore, the decrease in acid combination must be due to the formation of cysteic acid in the fibers. Cysteic acid forms a strong

Table 6.18 Acid-combining capacity of bleached hair

Sample description	Acid combining capacity[a] mmole/g hair	Cysteic acid mmole/g hair
Control (unbleached)	0.67	0.03
1 bleach	0.60	–
2 bleaches	0.52	–
3 bleaches	0.48	–
4 bleaches	0.43	–
Frosted hair	0.30	0.66

[a]Determined by the method of Maclaren [117]

ionic bond with the basic amino acid residues and in that manner inhibits their interaction with weaker acids, such as formic acid, thus decreasing the uptake of orange II dye.

Since the exocuticle and its A layer (see Chaps. 1 and 2) are highly cross-linked with cystine [125] and are near the fiber surface, one would expect a large increase in cysteic acid in the cuticle and, in all probability a decrease in the isoelectric point of hair. Thus a decrease in acid dye combination and an increase in the combination of cationic substances at or near the fiber surface occurs with increased bleaching or oxidative weathering.

Sagal [121] suggested that the acid-combining capacity of hair increases with permanent waving. Robbins [119] could not find a change in the acid-combining capacity of human hair waved under "normal" conditions on live heads. Both of these studies involved determinations on whole fiber. A "surface" analysis method might be more sensitive to such a difference, if it actually exists.

Modification to the number of acidic and basic groups have been made by Laden and Finkelstein [126], who added Bunte acid groups to hair, and by Robbins and Anzuino [127], who added polydimethylaminoethyl methacrylate groups to hair by in situ polymerization.

Robbins [128] demonstrated that the acid-combining capacity of human hair decreases with weathering, although only to a small extent. This study involved a comparison of root and tip ends of five samples of long hair (longer than 18 in.) that was visually lighter in the tip ends than the root ends. The acid-combining capacity varied from approximately 3% to 13% less in the tip ends. The most severely affected sample was hydrolyzed and analyzed for amino acids and found to contain significantly less lysine and histidine and a larger amount of cysteic acid in the hydrolyzates of the tip ends (see Table 6.19). This result is presumably from photochemical degradation.

Most of the subject matter in the following section on reaction conditions and the combination of hydrogen ions with hair has been studied thoroughly for wool fiber and confirmed in a few critical experiments with human hair.

Table 6.19 Acid combining capacity of root and tip ends of human hair

Sample description		% difference (tip minus root)
A		−9.9
B		−2.9
C		−12.9
D		−6.0
E		−2.9
		Average = −7.0%
	mmole/g hair	
	Root ends	Tip ends
Total basic amino acids[a]	0.75	0.69
Acid-combining capacity[b]	0.70	0.61
Cysteic acid[a]	0.02	0.04

[a]Via hydrolysis and amino acid analysis [119]
[b]Via method of Maclaren [117]

6.8.1.4 Reaction Temperature

Steinhardt et al. [122] studied the effect of temperature on the reaction of wool fiber with hydrochloric acid from 0°C to 50°C and found only small differences in the titration curve over the pH range where acid combines with wool. Heats of dissociation, from their titration data, are only 2,500 calories at 0–25°C, in good agreement with those for the back titration of carboxyl groups of simple acids and of soluble proteins.

6.8.1.5 pH and the Isoionic and Isoelectric Points

The pH at which a protein or particle has an equivalent number of total positive and negative charges as determined by proton exchange is the isoionic point. The pH at which a protein or a particle does not migrate in an electric field is called the isoelectric point. The isoionic point is a whole fiber property of hair and is reflected in the equilibrium acid–base properties of the total fiber; the isoelectric point is related to the acid–base properties of the fiber surface.

The isoionic point of human hair may be evaluated from titration data in the presence of salt (see Fig. 6.13) or buffers. Allowing thoroughly rinsed hair to equilibrate in deionized water and determining the pH of the resultant solution may also approximate the isoionic point. The isoionic point of wool fiber was determined by Steinhardt and Harris to be at pH 6.4 [116]. The isoionic point of

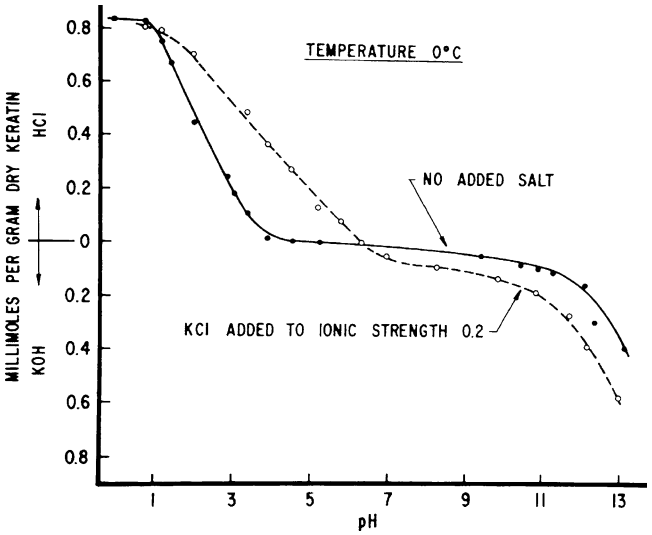


Fig. 6.13 The influence of salt on the combination of simple acids and base with keratin fibers (From data by Steinhardt, Fugitt and Harris [122])

human hair is close to that of wool fiber (generally near pH 6.0) and it varies among hair of different individuals. Freytag [129] found isoionic points from pH 5.6 to 6.2 by following the pH changes of hair in buffer solutions. An isoionic point of pH 5.8 plus or minus 1.0 was found for unaltered hair from nine different individuals, in a study by Robbins.

Wilkerson [68] found the isoelectric point of a single hair sample to be pH 3.67 by measuring the electrophoretic mobility of hair particles in buffer solutions. Parreira [130] found the isoelectric point of hair to vary from 2.45 to 3.17, while Harris and associates found the isoelectric point of wool fiber to vary between pH 3.4 and 4.5 [131, 132].

Capablanca and Watt [37] examined wool fiber that had been washed with detergent and extracted with various solvents using a streaming potential method to estimate the effect of free lipid on the isoelectric point of wool fiber. These scientists found an appreciable effect of free lipid on the isoelectric point. The surfactant washed wool (containing the most free lipid) provided an isoelectric point of 3.3 while the most effective lipid solvent extracted hair provided an isoelectric point of 4.5. These data show that the true isoelectric point of the surface hair proteins is close to 4.5 and that free lipid which contains fatty acids is an important and essential component of the surface of animal hairs. So, the more free lipid that is present in these surface layers, the lower the isoelectric point of the keratin fibers. Therefore, free lipid is important to the isoelectric point of hair and to the adsorption of surfactants or all ingredients onto human hair and the longer interval between shampoos the more free lipid in these layers and the lower the isoelectric point.

Similar isoelectric points for hair and wool fiber are to be expected, since chemical compositions of the cuticle (see Chap. 2) are similar and because both fibers show similar dye staining characteristics. Cuticle from both fibers stains more readily with cationic dyes than with anionic dyes [96], whereas the cortex stains readily to anionic dyes [133]. Since bleaching increases the ratio of acidic to basic amino acids [134], the isoionic point should decrease with increasing oxidation. One might also anticipate a similar decrease in the isoelectric point of hair with bleaching, since the epicuticle and A layer of the cuticle cells is rich in cystine.

For longer-term interactions, if the pH of the surrounding solution is below the isoionic point of hair, the hair will pick up acid, and above its isoionic point, it will attract hydroxide ions more readily. For short-term and surface interactions, the isoelectric point is more important than the isoionic point. The isoionic point becomes more important to whole-fiber treatments such as perms and bleaches and to longer time reactions.

In the absence of added salt, over the pH region of 4–9, there is negligible combination of simple acids or alkalis like hydrochloric acid or sodium hydroxide with wool or hair [116]. This phenomenon is not observed with soluble proteins and seems strange, since unbuffered solutions (near neutral pH) in the presence of hair that is free of acid or alkali drift toward the isoionic point of hair. The explanation is that in the presence of small solution-to-hair ratios (100 to 1 or less), the consumption of relatively small amounts of alkali or acid by the hair will provide a

significant pH drift in the solution. In addition, in most cases, salts are present in the solution leading to greater interaction.

6.8.1.6 The Influence of Anions on the Combination of Hydrogen Ions with Hair

Table 6.15 illustrates anion affinities of several acids by Steinhardt et al. [75] and shows that simple anions like chloride and ethyl sulfate have low affinities for hair. On the other hand, surfactant anions, such as dodecyl sulfate or dodecyl sulfonate, and dye anions (Orange II) have relatively high affinities. In fact, the anion affinities of Table 6.15 show a correlation ($r = 0.94$ and $r^2 = 0.90$) with molecular weight, suggesting that 90% of the variance can be explained by molecular weight. Since most of these anions differ primarily by increasing size of either aliphatic or aromatic substituents, this type of affinity may be associated with Van der Waals attractive forces and entropy. Therefore, the decreasing hydrophilic nature and increasing keratinophilic nature of these organic acids with molecular size cause the acid to partition from the aqueous phase to the hair phase.

6.8.1.7 Anions of Low Affinity

The effect of increasing chloride ion concentration in hydrochloric acid solution is to produce a greater uptake of acid by the fibers at any given pH below the isoionic point. Steinhardt et al. [116] demonstrated this effect for wool fiber and Robbins demonstrated it for human hair (see Table 6.20 and Fig. 6.13).

When one considers that essentially equivalent quantities of hydrogen and chloride ions combine with the fibers, it is apparent that the extent to which either one of these ions is taken up by the fibers will influence the other. The hydrogen ion has a greater influence on the combination of chloride ion with the fibers than chloride has on hydrogen, because hydrogen ion has a greater affinity for hair (see Table 6.20). However, since chloride ion does have some affinity for hair, increasing its concentration in solution does increase the combination of chloride—and ultimately hydrogen ions with hair or wool fiber.

Table 6.20 Influence of salt on the combination of acid with keratin fibers [116]

pH	Wool fiber[a]		Human hair[a]	
	25°C (No salt)	25°C (Ionic strength 0.2)	25°C (No salt)	25°C (Ionic strength 0.2)
1.0	0.78	0.83	–	–
2.0	0.44	0.73	–	–
3.0	0.15	0.51	0.29	0.46
4.0	0.03	0.29	–	–

[a]Data are expressed in mmole/g dry keratin and are interpolations from graphs from above references. Added salt is potassium chloride

6.8.1.8 Anions of High Affinity

A greater amount of protons or cations combines with hair or wool fiber, at acid pH, in the presence of anions of high affinity for hair [108, 113, 135]. In fact, the extent of combination at low pH (pH 2.5 or lower) can be in excess of the maximum combining capacity. This high affinity suggests that interaction between groups other than dibasic amino acid groups occurs with anions of high affinity. Interaction of the hydrophobic portions of the fibers with the hydrophobic group of the surfactant is involved, and protonation of amide groups has been suggested.

6.8.1.9 Competition of Cations of Low Affinity with Hydrogen Ions

In neutral dyeing or surfactant-hair interactions, competition of cations with hydrogen ions must play a role. When the concentration of hydrogen ions is low and cations of low affinity are present, the adsorption of anion is influenced by the concentration and affinity of cations for hair. If the cation affinity is high enough so that it is adsorbed, a counterion must accompany it to maintain electrical neutrality. In the presence of low-affinity cations, for example, sodium or potassium—hydrogen ions can be taken up until quite high pH values are reached [136]. However, competition between hydrogen ions and other cations will occur.

6.8.1.10 Competition of Cations of High Affinity

Long-chain quaternary ammonium compounds have a high affinity for human hair, and they compete quite effectively with hydrogen ions for sites on hair at acid pH in many creme rinse formulations. Furthermore, they are difficult to completely remove from hair with anionic surfactants.

6.8.1.11 Low Molecular Weight Organic Acids

The data of Table 6.21 suggest that the interactions of low-molecular-weight carboxylic acids with hair involve more than simply the back titration of the carboxylate groups. Many of these acids are relatively weak such as acetic, propionic, and butyric. Therefore, relatively high concentrations of these acids are required to achieve hydrogen ion concentrations approaching 0.1 M, the concentration of hydrochloric acid required for its maximum combining capacity. However, these acids at hydrogen ion concentrations well below 0.1 N produce extensive swelling, suggesting that the undissociated acid itself combines with the fibers [138].

Table 6.21 The interaction of carboxylic acids with human hair[a]

Acid used	pH	% Concentration	% Swelling (24 h)
Water	7.0	100.00	32
Hydrochloric	1.0	0.36	34
Formic	1.1	25.0	47
Formic	0.4	50.0	62
Formic	–	98.0	110
Acetic	1.15	50.0	47
Propionic	2.6	5.0	33
Propionic	1.4	75.0	54
Butyric	2.6	5.0	34
Butyric	1.65	75.0	46
Monochloroacetic	1.1	50.0	47
Trifluoroacetic	1.9	0.5	34
Trifluoroacetic	–	25.0	50
Trifluoroacetic	–	75.0	110

[a]Data from Barnett [137]

In the case of pure formic acid, extreme swelling results. However, the attraction for positive sites on the fibers must be greater for the anion of orange II dye than for formate ion, for Maclaren's acid combining test [117] to be valid. For additional discussion concerning this type of interaction, see Barnett's thesis [137] and articles by Speakman and Stott [123, 139].

6.8.2 Hydroxide Ion Interactions with Keratin Fibers

6.8.2.1 Maximum Alkali-Combining Capacity

The maximum alkali-combining capacity of keratin fibers from reaction with simple alkalis such as potassium hydroxide has been reported at 0.44 mmole/g for unaltered human hair [121] (no Correction for decomposition) and at 0.40 mmole/g for wool fiber [116]. This reaction involves the back-titration of the conjugate acids of amino and guanidino groups of the fibers, forming negative sites that attract cations.

6.8.2.2 Variation in the Alkali-Combining Capacity

Hair is more sensitive to alkaline hydrolysis than to acid hydrolysis, making this determination more difficult and complicated. Sagal [121] demonstrated a higher uptake of alkali in bleached hair and in permanent-waved hair than in cosmetically unaltered hair. This effect could be due to a larger number of acidic sites; however, it is likely also due to an increased susceptibility to hydrolysis for damaged hair.

6.8.2.3 Influence of Cations on the Combination of Hydroxide Ions with Keratin Fibers

Quantitative cation affinities have not been determined for human hair; however, Steinhardt and Zeiser [138] determined these for a series of quaternary ammonium halides. Their results were similar to those with anions, demonstrating increasing affinity for wool fober with increasing molecular size.

Organic ions of small size (below 150 Da) differ very little in affinity and are similar to inorganic alkali metal cations, but above 150 Da, the affinity of organic cations increases rapidly. The high affinity of hexadecyltrimonium (cetrimonium) and larger cations is due to ionic bonding plus Van der Waals attractive forces that with increasing size increases the hydrophobic nature of the molecule. Scott, Robbins and Barnhurst [140] demonstrated a similar phenomenon for human hair by comparing the sorption behavior of hexadecyl- and dodecyltrimonium bromides. These scientists found that under similar conditions of adsorption and desorption, greater amounts of the larger hexadecyltrimonium bromide combined with hair, attesting to its greater affinity.

Cations of low affinity, at high concentrations, increase the interaction of hydroxide ion with hair fibers. Steinhardt and Zeiser [138] described this phenomenon as an effect of salt on the base-binding behavior of wool. However, cations of high affinity produce an even greater effect in increasing the interaction of hydroxide ion with hairs [138].

6.8.2.4 Low Molecular Weight Organic Bases

Similar to the interactions of low-molecular-weight carboxylic acids with hair, the interactions of low-molecular-weight organic bases involve more than simply the back titration of conjugate acids with hair. Barnett [137] described the interaction of mono-, di-, and triethanol amines at 25% concentration and higher with human hair. The reactions of these species with hair involve extensive swelling and ultimately lead to decomposition and disintegration of the hair.

6.8.2.5 Interactions of Salts near Neutrality with Keratin Fibers

The interactions of surfactants and ionic dyes with keratin fibers, near neutral pH (5–8), have not been studied as thoroughly as acid and basic dyeing. However, Vickerstaff [141] suggested that the mechanism for neutral dyeing is analogous to the action of surface-active agents at an air/water interface, where they orient with their hydrophobic tail extending into the air and the hydrophilic group in the water. Another analogy is the electrophoresis of proteins in sodium dodecyl sulfate, where the hydrophobic portion of the surfactant binds to the protein and the charged group projects toward the solvent or gel.

Therefore, a mechanism for neutral interactions of surfactants with keratin fibers depicts the surfactant attaching to the fiber by its hydrophobic tail and the hydrophilic group that is the sulfonate group projecting toward the solution [142]. Robbins and Fernee [110] (see the discussion earlier in this chapter) provided evidence for a change in mechanism for the binding of surfactants to keratin as the pH of the system changes from acid to neutral.

Peters [136] proposed a "leading ion mechanism" for interactions near neutrality. For this mechanism, the fiber surface bears a net negative charge because of its low isoelectric point (pH 3.7). Positively charged ions are attracted to the negatively charged surface, thus helping to overcome the electrical barrier for anions. This view elevates the importance of the counterion (cations in particular) in neutral dyeing or surfactant binding to hair near neutral pH. The effect of salt addition on dye uptake is consistent with this mechanism, since the addition of electrolyte near neutral pH increases the amount of dye [143] or surfactant [144] that combines with hair fibers. Since anion and cation affinities are independent of pH [77], surfactants and dyes with high affinities bind readily to hair fibers even near neutrality. As mentioned before, a convenient rule of thumb is that anion or cation affinities increase with increasing molecular size of the organic moiety.

Most surfactant interactions with hair are above the critical micelle concentration (cmc), and aggregation introduces complexities to the above mechanisms. Sorption of sodium lauryl sulfate continues to increase above the cmc [145]. Therefore, higher concentrations of aggregate near the fiber surface may be capable of providing higher concentrations of monomer for diffusion into the fiber, because it is most likely monomer rather than aggregate that diffuses into the fiber. Interestingly, nonionic surfactant has been shown to decrease the sorption of sodium lauryl sulfate, probably by decreasing the cmc and thereby the concentration of monomer available at the surface. Ethoxylation to sodium lauryl sulfate decreases the sorption too, although it is not clear at this time whether this action is simply an effect on diffusion rate or on the anion affinity or both of these parameters.

6.9 Damage to Hair from Shampoos, Grooming, and Weathering

6.9.1 Hair Damage

Hair damage is the chemical and or physical breakdown or removal of structural components or parts of hair that either weaken it or make it more vulnerable to chemical or mechanical breakdown. Such damage occurs in shampooing and everyday grooming actions. Sunlight, pool water, and cosmetic products such as permanent waves, bleaches, straighteners, and some hair dyes chemically alter hair. These effects increase hairs propensity to further chemical and mechanical breakdown as shown by Swift and Bews [146] by an increased sensitivity to cuticle

abrasion/erosion and fiber splitting. To simulate or monitor hair damage, I conclude rubbing actions and impact loading in hair snags are more relevant to actual in-use damage and breakage of hairs than tensile testing with its abnormally low extension rate and because hair fibers will generally pull out under tensile loading rather than break, see Chap. 9 for details.

Shampoos can damage hair by abrasion/erosion and deformation during the shampoo process itself when hairs are rubbed against each other, or when deformed by bending, torsion and stretching while lathering, or while combing or towel drying or even when blow drying. Shampoos can also slowly dissolve or remove structural lipids and proteinaceous material from hair. Every time a person shampoos or conditions their hair, they either comb or brush it. Therefore, combing and brushing of hair and the resultant damage from these actions should be considered a part of the shampoo and hair-conditioning processes. This definition allows us to consider the fact that some shampoos prevent and reduce damage during these actions.

Okumura [147] suggested that a large amount of cuticle damage occurs in the lathering step during the actual shampooing of hair when fibers are rubbed against each other in the presence of detergents. Kelly and Robinson [148] concluded that shampooing and towel drying of hair also damages hair. However, these scientists suggested that combing and brushing damages hair more than the lathering step of shampooing, and further that brushing is more damaging than combing. They have also shown that cuticle loss is greater from wet combing than from dry combing. But in their analysis they did not consider whether some parts of the fiber are more vulnerable than other parts in wet versus dry combing or brushing such as root sections versus mid-sections versus tips.

6.9.2 Damage Involving Cuticle Fragmentation and Scale Lifting

Shampooing and grooming actions cause the cuticle to be more susceptible to further abrasion/erosion, to adhesion failure either in the cell membrane complex or inside cuticle cells and to the lifting of scales and other types of hair damage described in this section. These actions also lead to increased diffusion of chemicals into hair and to additional damage by penetrating chemicals or products.

Shampooing, combing and brushing and exposure to sunlight over time induce changes in hair that can be detected at the morphological level. These effects may be viewed as aging of hair (not the person) or of weathering damage. Chemical weathering effects include damage to hair by environmental factors such as sunlight, air pollutants, wind, sea water, or even chlorine in pool water. Several types of the following different actions produce rubbing of hairs against hairs or other objects that result in hair damage: combing and brushing, shampooing (during both the lathering and drying steps including towel drying or blow drying of hair), rubbing hairs during styling, such as curling, braiding and tying or clamping hairs together frequently in the same spot in a bun or a knot, and rubbing hairs against other hairs

while turning one's head during sleeping or lying down. All of these rubbing actions except the very last one are a part of the hair grooming process.

The process of cuticle chipping that results from rubbing objects such as grooming devices and especially rubbing hairs against other hair fibers is a major factor in hair damage (Fig. 6.14); also see the discussion in Chap. 1 on the different stages of cuticle wear over time. As indicated earlier, hair damage can be produced by either stretching or bending, by rubbing hairs, by hairs impacting against other hairs, by chemical action or even by penetration between the scales (intercellular route, see Fig. 6.6). For example, the lifting of scales can be produced by stretching (Fig. 6.15), by bending (Fig. 9.30) or by penetration of ingredients between the scales (Fig. 6.16).

Figures 6.17 and 6.18 illustrate that scale lifting occurs from stretching and bending actions during normal combing and brushing of hair. Removal of large sections or chunks of a single scale results from rubbing actions particularly after scales have been raised (Figs. 6.19 and 6.20). Scale breakage in these latter two figures was produced by the intra-fiber rubbing actions created by tying a hair fiber in a knot. This type of action, although not common on straight hair, can actually occur on hair fibers attached to the scalp and is more common with curly hair.

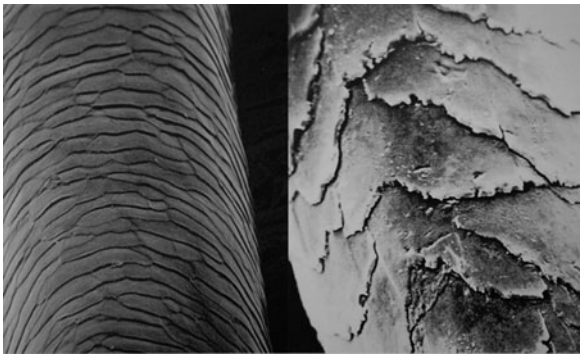


Fig. 6.14 SEMs illustrating damage from the chipping of scale edges. *Left*: SEM shows the fiber surface close to the scalp; note the smooth scale edges and faces. *Right*: SEM illustrates the fiber surface of about 1 year's growth and wear. Note the rough chipped and worn scales

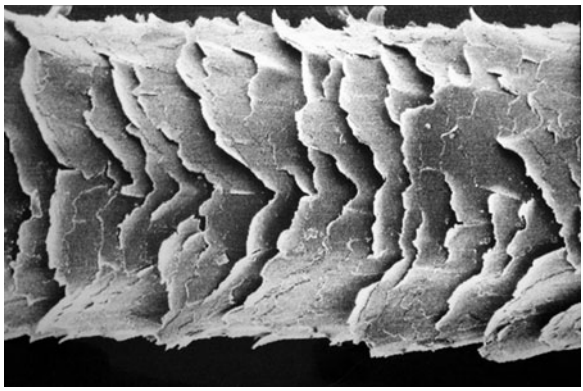


Fig. 6.15 Lifted scales from stretching at low RH (SEM provided by the courtesy of Sigrid Ruetsch)

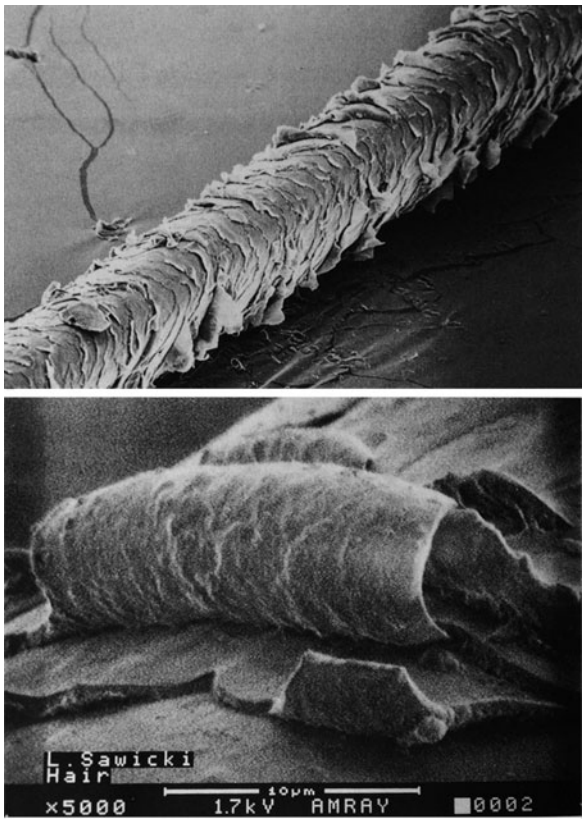


Fig. 6.16 Lifting of scales on permed-dyed hair by alternating treatments with TEA lauryl sulfate and stearalkonium chloride

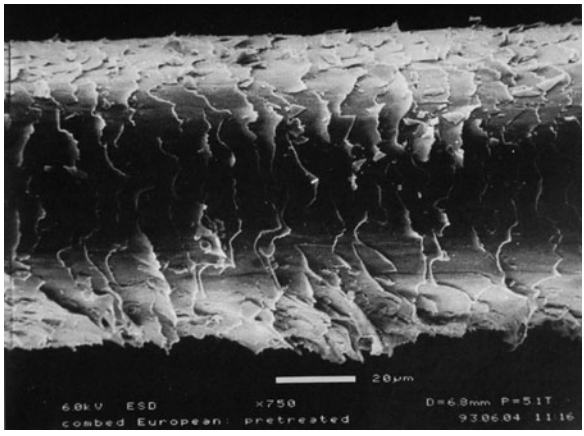


Fig. 6.17 Scale lifting caused by vigorous combing of hair tresses

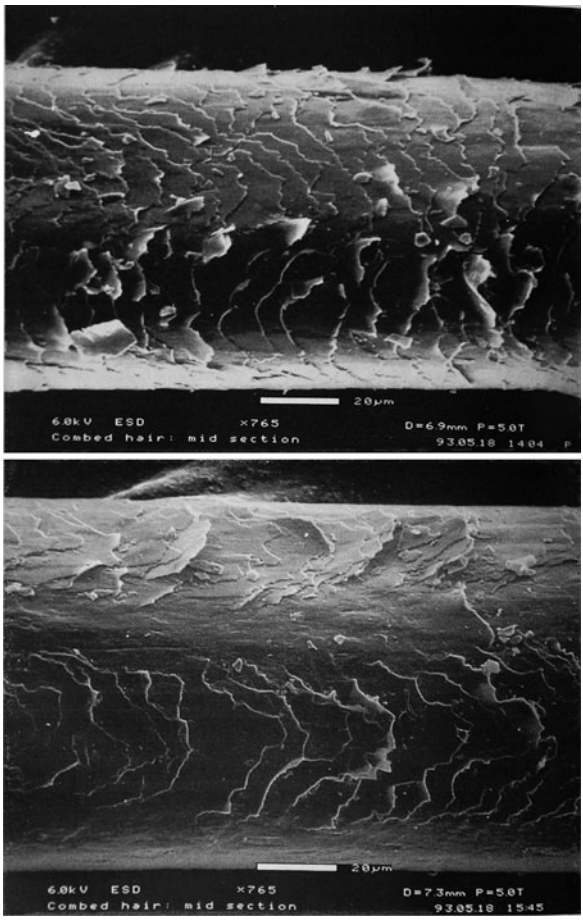


Fig. 6.18 Chipping, scale lifting and tearing of large sections of cuticle by vigorous combing

Shampooing or erosion can also remove lipid and even proteinaceous matter leaving the hair feeling dry and more susceptible to further damaging actions. Large segments or sections of scales can also be abraded, torn or ripped from the hair by combing actions, see Figs. 6.17, 6.18 and 6.21. The more severe abrasive damage is most likely to occur from back rubbing (teasing hair) or from combing hair while heat drying.

The uneven removal of scale sections also occurs by continuously rubbing against the same area on a hair as occurs in a twisted or noncircular fiber with a "high spot" (high region). See the section in Chap. 9 on fiber shapes. This type of effect can occur even when the rubbing forces are extremely low. For example by sliding a hair fiber under its own weight (only 0.58 mg) continuously (about 25 times) over two other parallel hairs wear patterns are actually produced, see Figs. 6.22 and 6.23. Combing hair can also produce a similar type of wear (Fig. 6.24). Rubbing actions as in back-combing or teasing hair can even induce

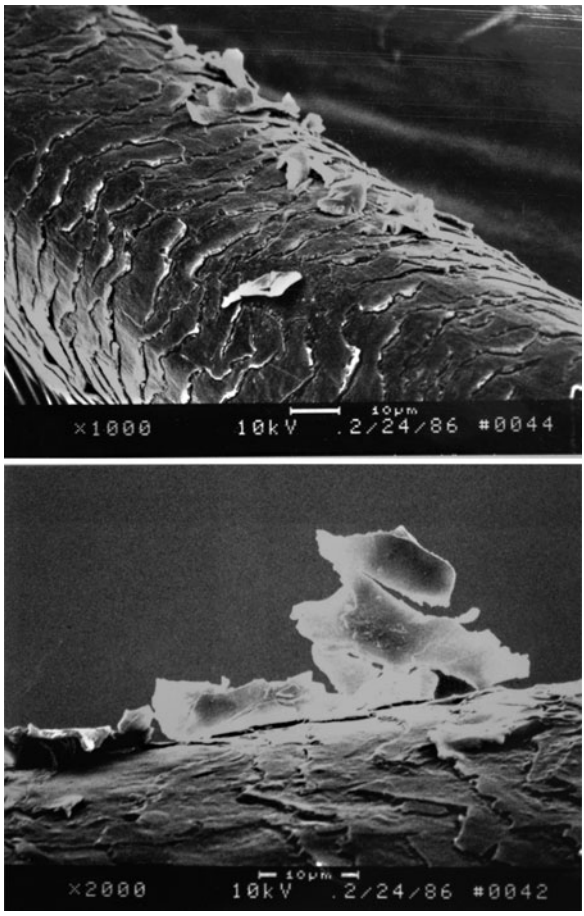


Fig. 6.19 Tearing or breaking off of large sections of a single cuticle scale after scale lifting

cortical lifting and damage to the cortex (Fig. 6.25). The foregoing types of damage can occur anywhere on the fiber, even near the root and mid sections of the hair and especially near the tips.

Garcia et al. [149] developed a mathematical model to predict cuticle wear, assuming that wear occurs primarily by cuticle chipping. These scientists concluded that cuticle erosion from grooming accelerates as the grooming operation moves closer to the tip end of the hair. This effect partly results from the fact that scale raising and removal of larger chunks of scales and even cortical lifting and other types of damaging action become greater as the grooming action moves closer to the tip ends because the cell membrane complex and other vital structures have been weakened more by longer exposure to chemical and physical actions near the tip ends. But, even more importantly, this type of tip end damage occurs because of end wrapping during dry combing which is discussed later in this chapter but in more detail in the section on hair breakage in Chap. 10.

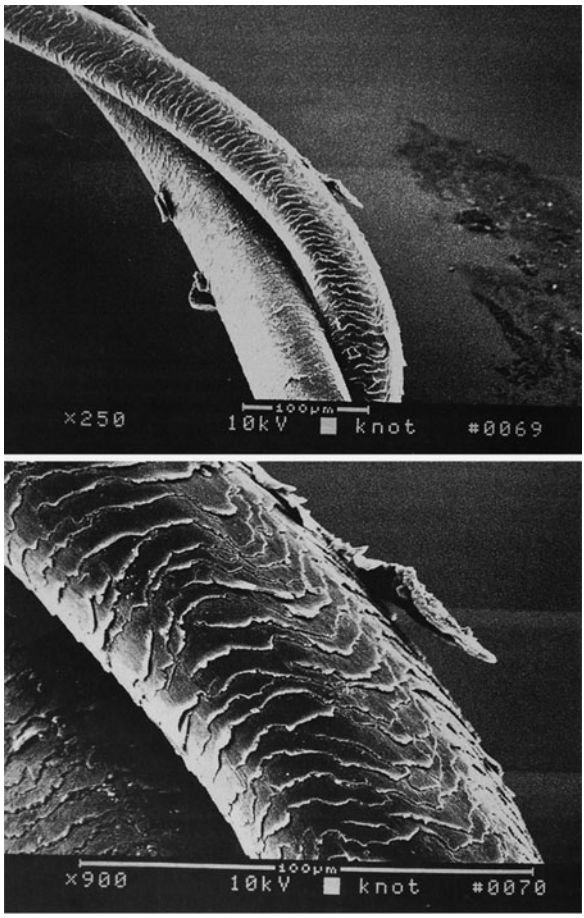


Fig. 6.20 Tearing of large sections of cuticle from hair on hair rubbing during knot formation

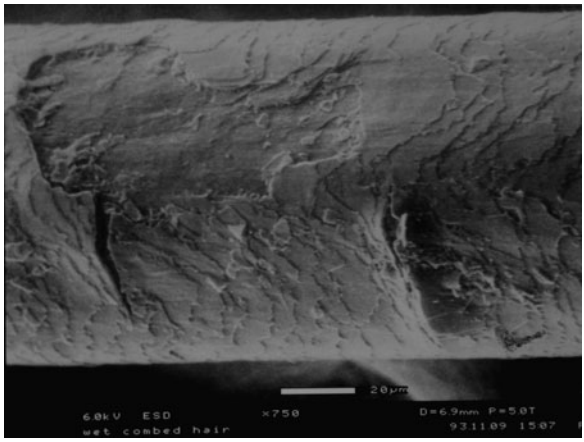


Fig. 6.21 Tearing of large sections of cuticle by vigorous combing of wet hair while heat drying

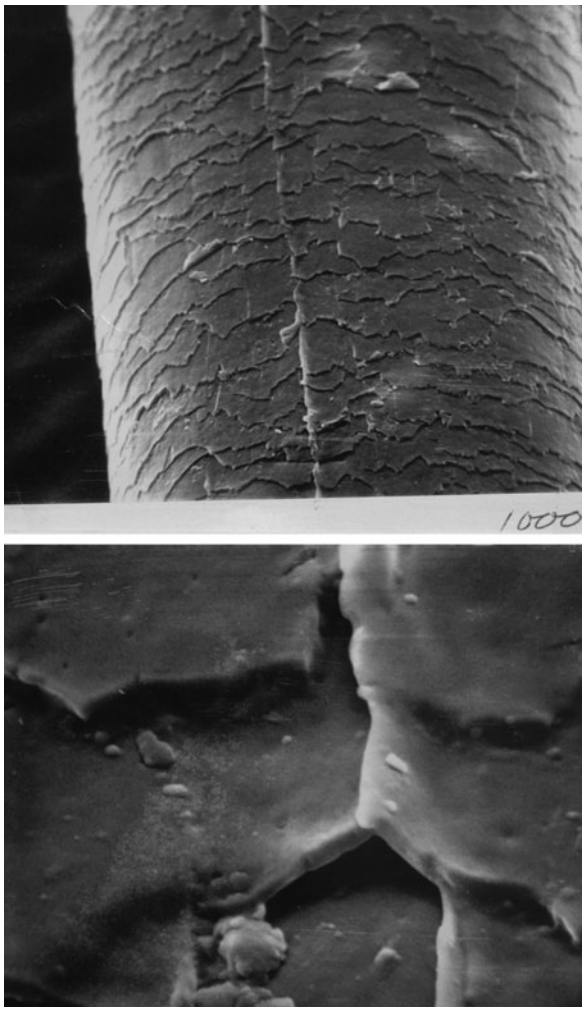


Fig. 6.22 Cuticle wear caused by sliding one single hair fiber (20 cm long) loop (wt. 0.58 mg) over two parallel fibers in a sliding friction experiment. See Chap. 9

In 1982, Kelly and Robinson [148] described the formation of split ends by the gradual erosion of cuticle scales during shampooing, drying, brushing and combing of hair (see Sect. 6.9.3 in this chapter and on hair breakage in Chap. 10). Kambe et al. [150] concluded similarly, that the loss of or the gradual fragmentation of cuticle cell layers results in split ends. Robbins and Sandu [151] took the method of Swift and Bews [152] for the physical isolation of hair cuticle and modified it to produce a method to quantitatively assess cuticle fragmentation or damage to the cuticle. Cuticle particles can be broken off and isolated from hair by shaking short sections of fibers (approximately 1 cm long) in water or even by wet combing of tresses (Fig. 6.26). These hair fiber fragments collected from wet combing or brushing of hair fibers have been proven to be fragments of hair by microscopic examination, by infrared analysis and by amino acid analysis. Silva et al. [153]

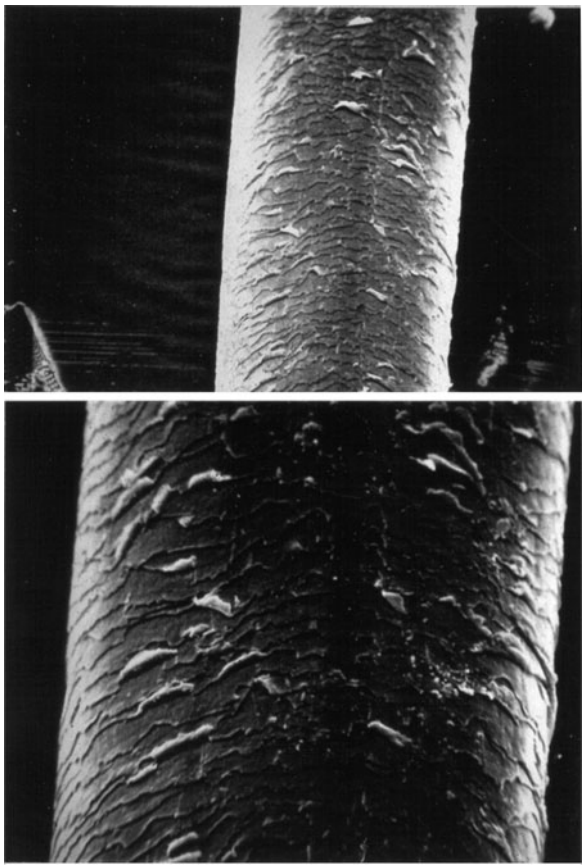


Fig. 6.23 Cuticle wear from a fiber from the experiment described under Fig. 6.22. Note the lines of wear and the folded back scale edges. This latter effect is from tip to root rubbing

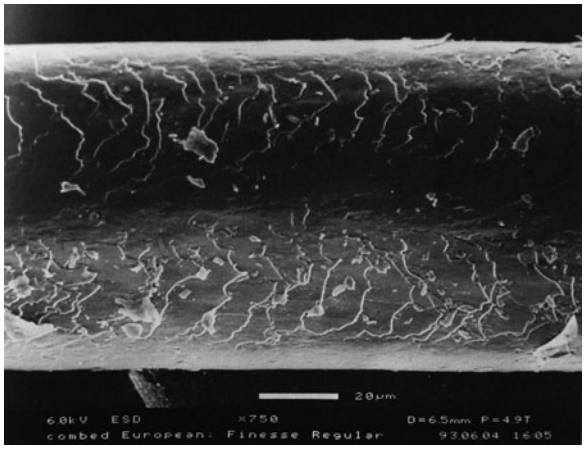


Fig. 6.24 Axial wear along a hair fiber from tress combing. This wear pattern is similar in type to that caused by the fiber loop experiment, illustrated in Fig. 6.22 (Micrograph provided by the courtesy of Elizabeth Gretler)

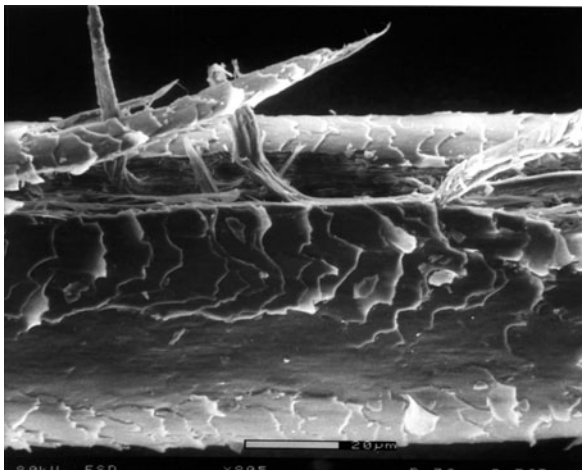


Fig. 6.25 Cortical lifting caused by back combing (teasing) of a tress (Micrograph provided by the courtesy of Elizabeth Gretler)

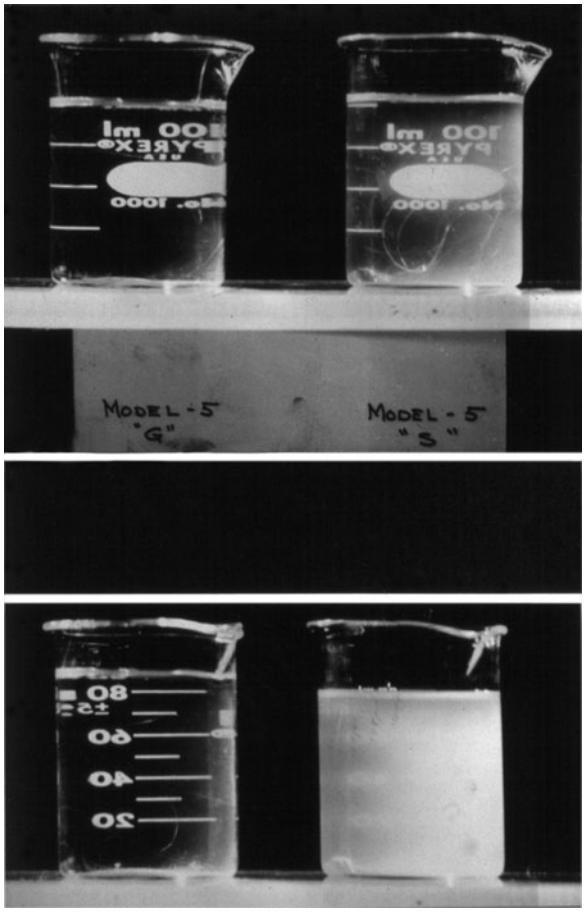


Fig. 6.26 Cuticle fragments collected from wet combing hair on heads and dipping the hair into water periodically (*G* is a conditioning shampoo and *S* is a cleaning shampoo)

recently modified and improved the colorimetric part of this analytic procedure of Robbins and Sandhu using the Bradford assay instead of the Lowry method.

Factors that accelerate cuticle wear and fragmentation are: hair swelling, increased rubbing, increased frictional resistance and damage to the cell membrane complex, the endocuticle or to other fiber components that make the surface layers more prone to swelling and the formation of cracks or scale lifting. Takahashi et al. [154] provided evidence that cuticle wear on Asian versus Caucasian hair occurs at different rates because of differences in the elasticity of the different layers inside cuticle scales. These scientists showed that the scales of Asian hair are removed faster by wet sonication or by bleaching the hair followed by shampooing and combing the hair over a large number of cycles. In the latter case after 90 times for four cycles fewer scales were found on the Asian hair relative to the Caucasian hair 3.2 versus 1.3 scales respectively. On further examination of the hair using an Atomic Force Microscopic probe to measure elasticity as a function of depth, these scientists found a greater difference in elasticity as a function of depth for the Caucasian hair (1.41 vs. 1.26). Takahashi et al. concluded that the scales of the Asian hair are more uniform inside and therefore more resistant to fracturing.

Takahashi et al. concluded that for wet cuticle fragmentation, the scales of Asian hair are removed by fracturing in the CMC (most likely in or near the central contact zone which has been shown to be hydrophilic), but Caucasian hair fractures inside the scales in the hydrophilic endocuticle. These mechanisms are consistent with the hypothesis of Robbins et al. [155] that wet fractures occur more readily in hydrophilic regions while dry state fractures are more prone to form in hydrophobic regions.

A schematic representing a mechanism for wet and dry state cuticle fragmentation is depicted in Fig. 6.27. For wet fragmentation, the first step involves swelling of the cuticle followed by the formation of cracks primarily in the endocuticle [155] or even the hydrophilic parts of the cell membrane complex [154]. These damaging actions result in enhanced swelling and a greater amount of hair fragmentation. This mechanism also shows that subsequent treatments can lead to either enhanced fragmentation by either dissolving non-keratin material or through additional cracking that produces cuticle lifting and distortion or conversely some ingredients can even strengthen the cuticle and inhibit fragmentation, possibly through adhesive bonding. For additional discussion on this latter subject see Chap. 9.

The fact that swelling of hair contributes to wet cuticle wear has been demonstrated in many different ways. For example, shaking of hair fiber snippets in water produces greater fragmentation than compared to shaking hair in chloroform or other non-swelling solvents. Similarly, for permanent waved or bleached hair versus virgin hair, the more damaged the fibers the more swelling and more fragmentation. The effects of increased rubbing have also been demonstrated in a number of ways. The simplest of these is the fact that more fragmentation occurs with a greater number of comb or brush strokes and for dry combing greater fragmentation occurs in tip ends versus root sections of hair.

The effects of increased frictional resistance also leads to more fragmentation as demonstrated by comparing shampoos to cream rinses or different conditioning shampoos, that usually (but not always) provides for greater fragmentation and

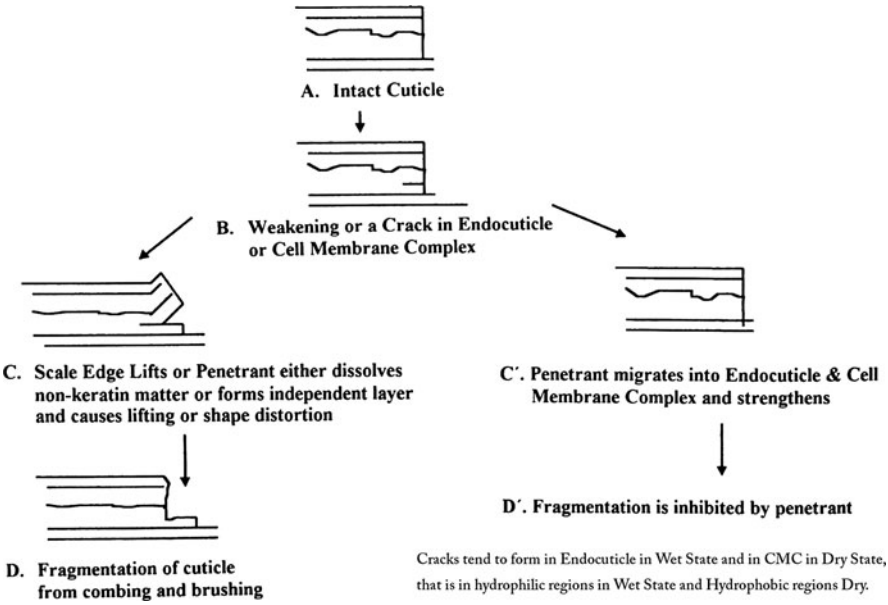


Fig. 6.27 Schematic diagram illustrating the process of cuticle fragmentation

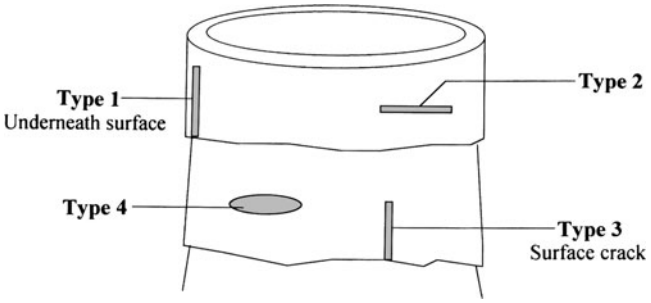


Fig. 6.28 Different types of cuticle cracks shown to form in human hair fibers

higher frictional resistance [156]. Weakening or cracks in the cuticle also leads to more fragmentation. To date, at least five different types of cuticle cracks have been demonstrated. The first four of these are cracks in the cuticle (Fig. 6.28) while the fifth is through the cuticle and the cortex.

Figure 6.29 illustrates the hair surface of a non-cracked cuticle taken from mid-sections of hair in relatively good condition. The crack that is parallel with the fiber axis and in the plane of the cuticle layers (type 1 in Fig. 6.28) has been demonstrated by many different groups and consists of two essential types (Figs. 6.30 and 6.31). The most common of the Type I crack forms in the dry state and it occurs in the cell membrane complex between the upper Beta layer and

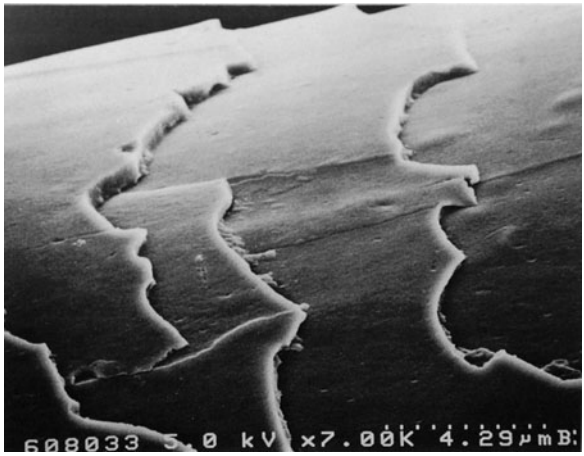


Fig. 6.29 Lightly damaged control hair surface. No cuticle cracks or lifting (SEM kindly provided by Sigrid Ruetsch)

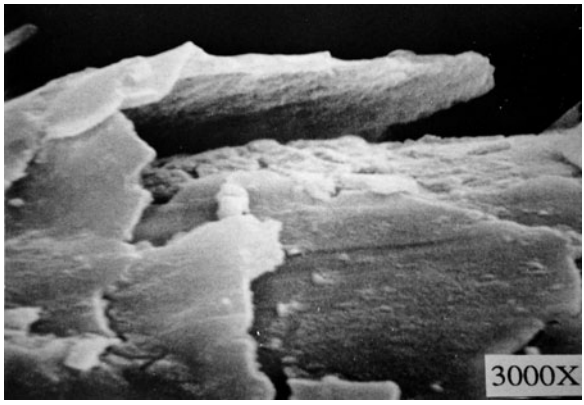


Fig. 6.30 Crack in the endocuticle formed from extending untreated hair (Type 1 crack) (SEM kindly provided by Sigrid Ruetsch)

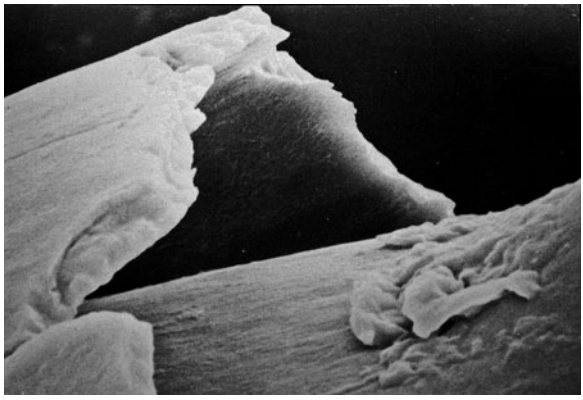


Fig. 6.31 Crack in the cell membrane complex formed by extending hair fibers wet. Note the smooth surfaces of the crack versus the rough surfaces of the endocuticular crack in Fig. 6.30 (SEM kindly provided by Sigrid Ruetsch)

the Delta layer and is called Beta-Delta failure, see Fig. 6.31. This type of crack has been described in detail by Feughelman and Willis [157].

In general, if the hair is in good condition and the fiber is extended at a very slow rate in the wet state or at high RH [158, 159] cracks can form in the endocuticle leaving a relatively rough appearing endocuticle on the bottom surface of the crack (Fig. 6.30). On the other hand, if the fiber has been damaged chemically, since one of the main sites of chemical attack is the cell membrane complex, cracks may appear in that region leaving a relatively smooth surface at the bottom of the crack (Fig. 6.31). Reutsch et al. [158, 159] described details of the formation of these two cracks and some attempts to reduce or eliminate their formation. These scientists also discuss how the lifting of cuticle scales leads to increased cuticle removal or cuticle fragmentation.

Cracks perpendicular to the fiber axis (type 2, Fig. 6.28) may also be produced by stretching hair fibers in water or at high humidities at more common extension rates (including cyclic extension actions) (see Fig. 6.32). Extension of hair fibers to 30% in water does not produce Beta-Delta failure, but it can produce multiple circumferential fracturing with separation of cuticle sections from the cortex, see Fig. 6.32 [160, 161]. However, this type of failure can occur at lower extensions during cyclic extension. This type of failure originates at the junction of the cuticle and the cortex and is induced from swelling pressure by the cortex at this boundary because the cortex swells more than the cuticle in water. This swelling pressure on the cuticle working in conjunction with extension forces initiates a crack in the cuticle at the cuticle cortex boundary that propagates through several cuticle layers.

Long term sunlight exposure can create brittleness in the cuticle which is revealed by tensile extension after extensive sun exposure (Fig. 6.33). The crack shown in Fig. 6.32 is from extension cycling. The sunlight exposure for the fibers depicted in Fig. 6.33 is beyond normal exposures, however, these cracks are of a

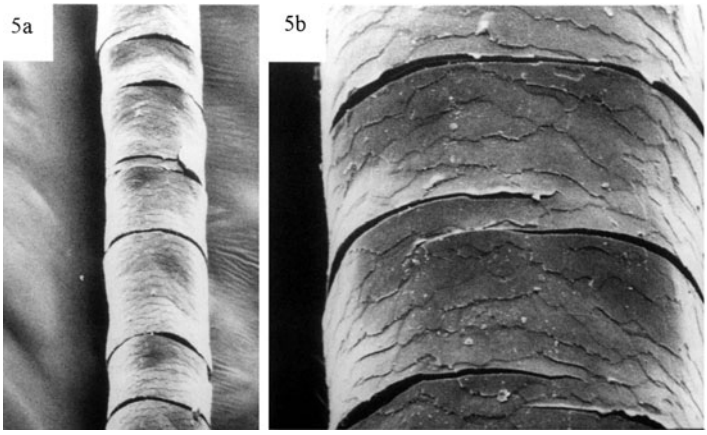


Fig. 6.32 Severe transverse cuticle cracks (Type 2) from extension cycling by Gamez-Garcia [160] (Reprinted with permission of the Journal of the Society of Cosmetic Chemists)

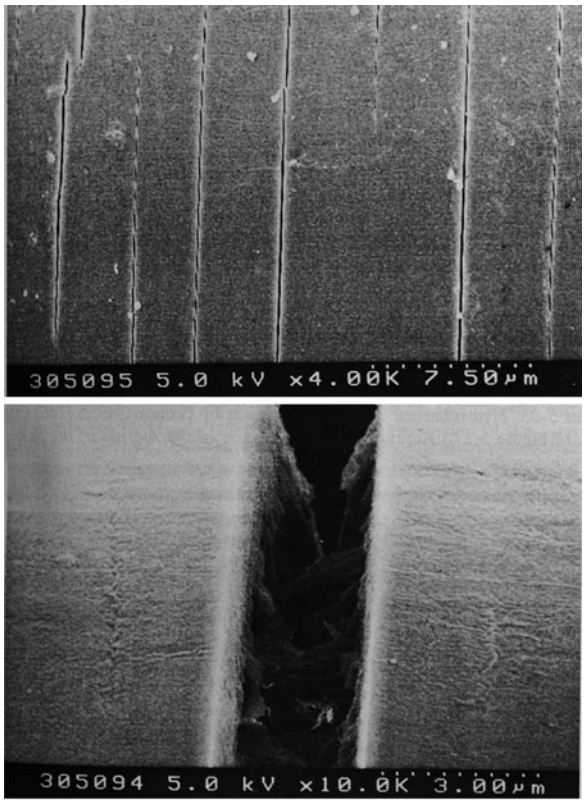


Fig. 6.33 Transverse cracks in the cuticle (Type 2 crack) from long term uv-exposure at high RH and extension (SEM kindly provided by Sigrid Ruetsch of Textile Research Institute)

macro scale, that is several microns long. It is likely that under normal exposures, related weaknesses on a micro scale (orders of magnitude lower) are created in the fiber by sunlight exposure and stretching and these defects ultimately lead to increased cuticle fragmentation.

Another interesting cuticle crack (type 3, Fig. 6.28) was first demonstrated by Gamez-Garcia [161] (Fig. 6.34). This crack occurs parallel with the fiber axis (Fig. 6.34, left side), but is perpendicular to the cuticle layers and is generally associated with heat drying hair. This type of crack tends to occur only in the uppermost exposed cuticle layer and is associated with the relief of pressure by the rapid removal of water from the surface cuticle layer producing these straight surface cracks. That these cracks result in increased cuticle fragmentation is illustrated by the electron micrograph of Fig. 6.34 (right side) showing exposed endocuticle remaining after grooming actions have removed cuticle in the vicinity of the cracks. The exposed endocuticle suggests that crack initiation is either in the swollen endocuticle or at the endocuticle-exocuticle boundary.

A fourth type of crack has been demonstrated by Gamez-Garcia [160] and by others (Fig. 6.35). This crack appears as irregular ovoidal or bubble type cracks or craters through several cuticle layers. Gamez-Garcia attributed this effect to thermal and extension cycling. We observed a similar but larger crack from combing wet hair while heat-drying (Fig. 6.36) which may be viewed as thermal and

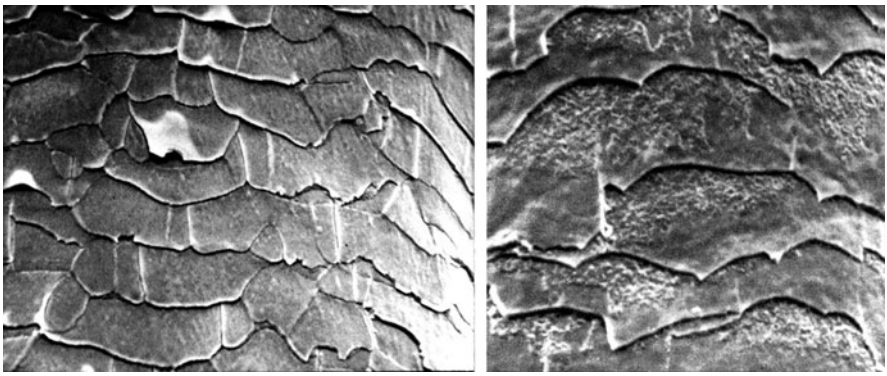


Fig. 6.34 Hydrothermal cracks in the cuticle from heat drying by Gamez-Garcia [161] (Type 3). *Left*: These cracks were produced by heat drying. *Right*: The same heat dried tress was combed producing this type of damage (Reprinted with permission of the Journal of the Society of Cosmetic Chemists)

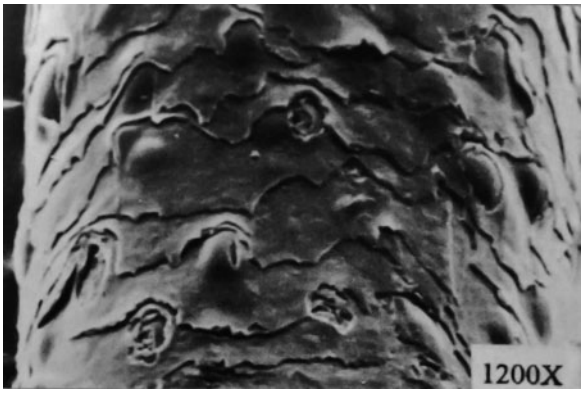


Fig. 6.35 Deep ovoidal cuticle cracks produced by thermal and extension cycling treatments by Garcia [149] (Reprinted with permission of the Journal of Cosmetic Science)

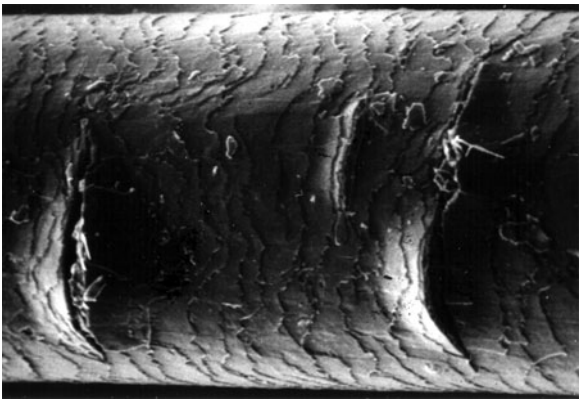


Fig. 6.36 Deep ovoidal cuticle cracks produced by vigorous wet combing and heat drying of hair

extension cycling. This crack is most likely related to a combination of cyclic extension actions that result from heat drying and combing hair and the relief of pressure from the escape of water from the hair during blow drying. McMillen and Jachowicz [162] reported significant damage to hair from the use of curling irons; however this damage has not been characterized microscopically. The fifth type of crack is a deep splinter type crack usually produced by teasing or back combing (Fig. 6.25). This type of crack is very deep and proceeds through all cuticle layers into the cortex.

Thus, weakening of cuticle layers by sunlight and or chemical treatments and cyclic deformations results in increased swelling or even cracks in the cuticle and ultimately to increased fragmentation. These effects initially are subtle damaging actions. The cosmetic industry has come to understand these effects better today than in prior years and we are gaining a better grasp on how to prevent or minimize these damaging actions. For more details on this subject, see Chaps. 9 and 10.

The mechanism presented for cuticle fragmentation (Fig. 6.27) shows that when the cuticle cell membrane complex or the endocuticle have been weakened or cracked the hair is more vulnerable to penetrating chemicals that can either promote or inhibit fragmentation and to grooming forces that can exacerbate fragmentation. Much of the ensuing discussion illustrates hair fragmentation, while the latter effect is described in more detail in Chap. 9.

While studying cuticle fragmentation and the buildup of surfactants on hair, we came across another interesting phenomenon involving scale lifting. We observed that scale lifting and scale distortion occurs on some hair fibers treated with alternating treatments of specific anionic and cationic surfactants. Figure 6.37 illustrates a control hair fiber used in these experiments, both in the wet (top) and dry (bottom) state that does not exhibit this effect. Figure 6.38 illustrates this scale lifting phenomenon in the wet state and Fig. 6.16 depicts this effect in the dry state. This scale distortion (Fig. 6.16) was actually produced in a half-head study on a live head. Figure 6.39 produced on a subject in a half head study shows how scale lifting dulls the hair. In this experiment alternating treatments of stearalkonium chloride and triethanol ammonium lauryl sulfate produced the scale lifting (Fig. 6.16) on the models right side (Fig. 6.39). While the control side (model's left) was treated with stearalkonium chloride and sodium deceth-3 sulfate where no scale lifting was observed.

A wide range of cationic and anionic surfactants were examined in this scheme and different types of hair were used to try to gain some insight into the mechanism of this phenomenon. For hair types, we observed that permanent waved hair produced this effect more readily than virgin hair and that permanent waved hair treated with oxidation dyes was even more susceptible. In addition, hair permed on the head produced lifting more readily than hair permed in the laboratory. Further, the more stringent the permanent waving conditions, the more readily lifting occurred. The effect could be observed on bleached hair, but not as readily as on permed hair. These results led to the conclusion that permanent waving or reductive damage to the cell membrane complex is important to this scale lifting effect.

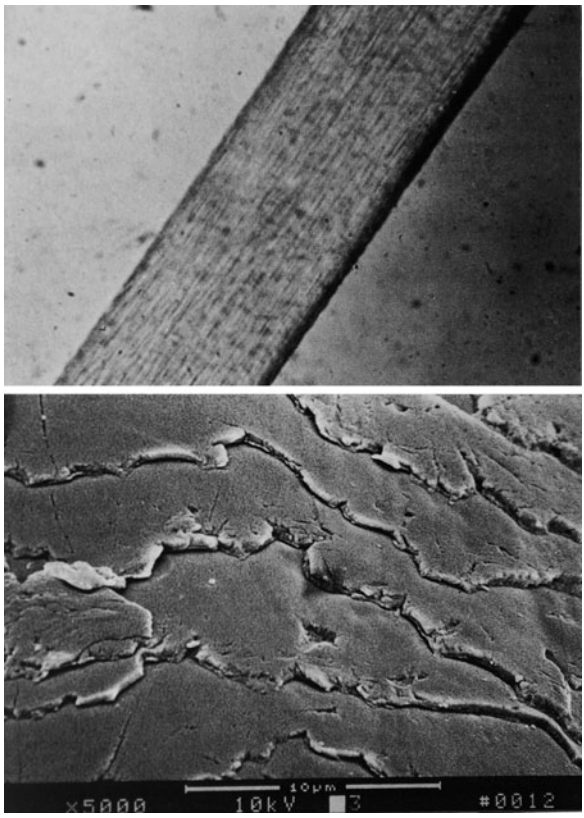


Fig. 6.37 Control fibers for penetration/deposition experiments. *Top*: Light micrograph in the wet state. *Bottom*: SEM illustrating the dry fiber surface

For cationic surfactants, we observed that lifting could be produced more readily by cationic surfactants alone such as stearalkonium chloride or cetrimonium chloride than by formulations containing both cationic and specific neutral conditioning agents such as cetyl or stearyl alcohol in addition to the cationic. Furthermore, the higher the ratio of lipid to cationic material in the conditioner formulation, the fewer tendencies for this scale lifting to occur. For anionic surfactants, dodecyl alcohol sulfates were very effective for producing lifting. Changes to the alcohol sulfate molecule that increase its water solubility and decrease its penetration rate such as ethoxylation tended to reduce scale lifting. But, decreasing the size of the sulfate molecule to eight carbon atoms (with no ethoxylation) increased its ability to penetrate inside the fiber and at the same time increased the tendency for scale lifting (Fig. 6.40). Scale lifting could not be induced by the anionic alone. The interaction of the anionic with the cationic surfactant by alternating treatments was necessary to produce this scale lifting.

We concluded that formation of a cationic-anionic complex inside either the endocuticle or the cell membrane complex is necessary to produce this effect. If these parts of the fiber are damaged, for example, by permanent waving, then penetration is enhanced. Adsorption of the cationic species occurs inside the cell

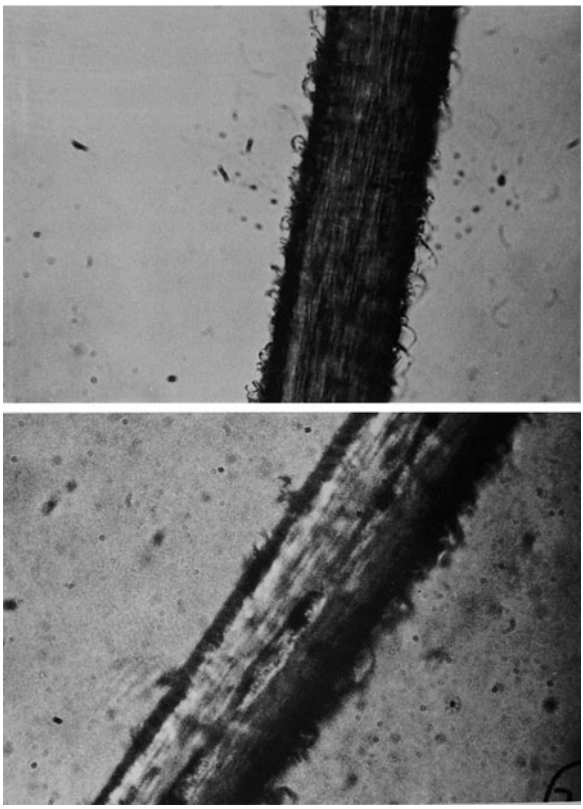


Fig. 6.38 Scale-lifting (in the wet state) by alternating treatments of TEA lauryl sulfate and stearalkonium chloride. Hair previously permed on a live head and subsequently treated in the laboratory

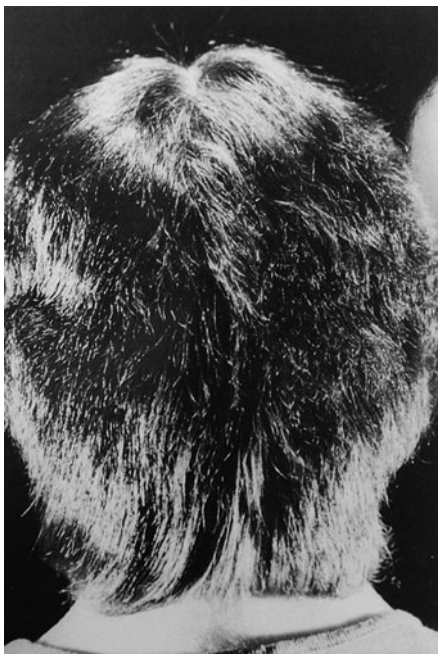


Fig. 6.39 Half head experiment. The *right side* was treated with alternating treatments of TEA lauryl sulfate and stearalkonium chloride. The *left side* was treated with sodium deceth-3 sulfate and stearalkonium chloride. Note the shine on the left side and the dullness on the right. This hair was originally permed and oxidatively dyed on the head of a panelist and worn for several weeks before the main treatment

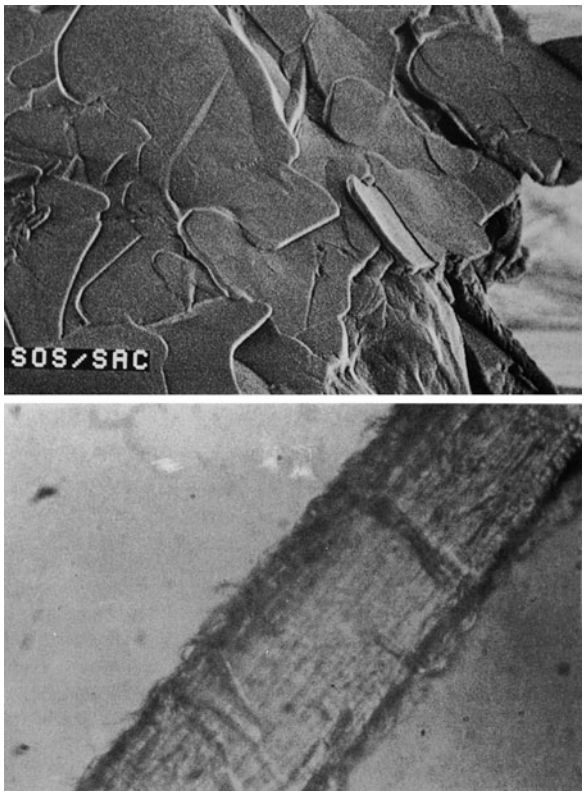


Fig. 6.40 Hair fibers treated in the laboratory with alternating treatments of sodium octyl sulfate and stearalkonium chloride. *Top*: SEM illustrating dry state effects. Note the scale damage and the large deposits. *Bottom*: Light micrograph illustrating the appearance of the fiber wet. Compare to controls illustrated in Fig. 6.37

membrane complex and the endocuticle. On washing with the anionic surfactant, penetration occurs and an insoluble cationic-anionic complex deposits inside the hair. After a sufficient amount of this insoluble complex forms in the cuticle, it creates a hydrophobic layer and scale lifting can occur. Scale lifting in this case is caused by differential adsorption and release of water by the differences in the moisture binding levels of the different layers of the cuticle cell. This produces a bending or lifting action similar to the effects of a thermostat from its reaction to heat and differences in thermal conductivity of its layers. Scale lifting by this mechanism leads to greater cuticle fragmentation.

To study the effects of scale lifting we employed a variety of techniques including light scattering. C. Reich made the observation that hair fibers exhibiting scale lifting or scale distortion will show a decrease in reflectance at the specular angle and an increase in the scattering of light at higher angles (Fig. 6.41). F. Schebece constructed a fiber holder for the goniophotometer that permitted treatment in the holder so that before and after measurements could be made on the same spot on the fiber. These same fibers could then be examined microscopically after light scattering measurements. Using this technique in combination with scanning electron microscopy we were able to detect scale lifting caused by the penetration-deposition mechanism from a few shampoos and conditioners and other

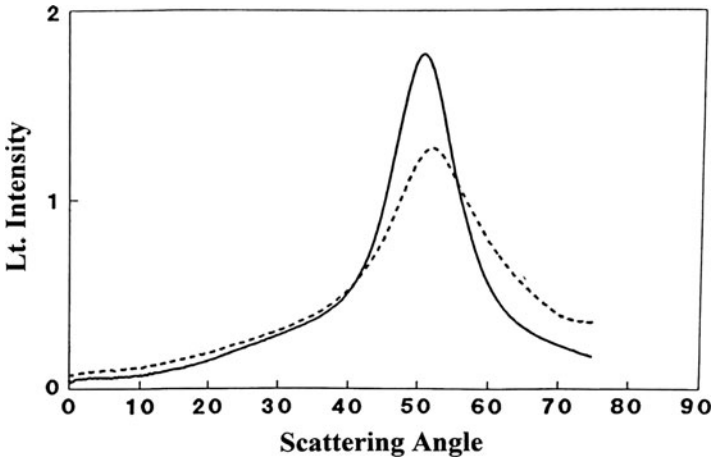


Fig. 6.41 Schematic of light scattering curves illustrating a normal untreated hair fiber (*solid line*) and a fiber with scales lifted (*dashed line*)

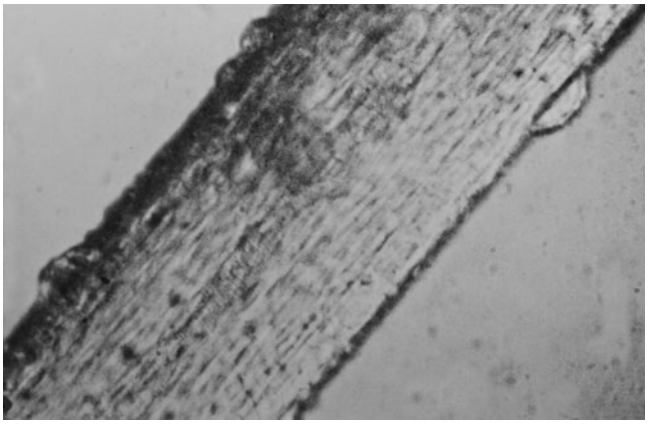


Fig. 6.42 Light micrograph of hair in water illustrating scale lifting caused by alternating treatments of a cleaning shampoo and a leading US hairspray

hair products in the marketplace. Several commercial products were capable of causing scale lifting on permed-dyed hair. A leading US hairspray (Fig. 6.42), several alcohol sulfate based shampoos when used with a few conditioners (containing a high ratio of cationic to neutral or lipid conditioning agents), and a leading 2 in 1 shampoo (Fig. 6.43) were all shown to be capable of causing scale lifting when used on hair that had been permanent waved and dyed on the scalp. These experiments demonstrated the effects of the penetrating agent forming a damaging layer most likely inside the cell membrane complex or the endocuticle and causing scale distortion and lifting as described by the mechanism in Fig. 6.27.

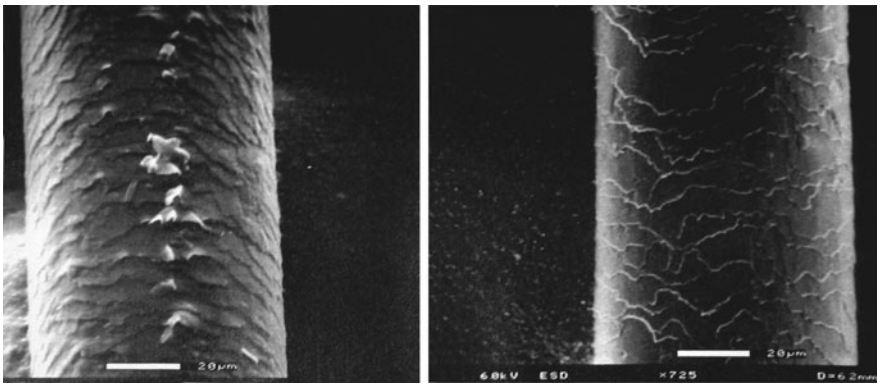


Fig. 6.43 Scale lifting by a leading US 2 in 1 shampoo. *Right*: Control treatment by a 2 in 1 shampoo that does not cause scale lifting. *Left*: The US 2 in 1 shampoo that caused scale lifting. This formula is no longer being sold

Another interesting technique for artificially generating scale lifting and splits has been described by Kon, Nakamura and Takeuchi [163]. This technique involves extraction of proteins from the fiber via enzyme digestion followed by freeze drying. This method has been used to study hair damage prevention by polymers.

6.9.3 Fracturing Hair by Tensile Extension

One important paper on the fracturing of human hair by tensile extension was published by Henderson et al. [164] and two by Kamath and Weigmann [165, 166]. These scientific studies show that breaking or fracturing of hair fibers under tensile extension occurs differently in the cuticle versus the cortex and fracturing of hair fibers occurs in different patterns. Furthermore, these fracture patterns depend on the type of hair, the relative humidity and whether or not the fiber is twisted or contains flaws. The section below and the sections on elastic and tensile deformations in Chap. 9 and on hair breakage in Chap. 10 provide additional details on this subject.

When the hair has not been chemically or physically damaged and it is below 30% RH or above 90% RH, it tends to fracture most often in the smooth fracture pattern (Figs. 6.44 and 6.45). The origin of the fracture (Fig. 6.44) is at the cuticle-cortex junction (lower portion of the photograph). The fracture then propagates from this point across the fiber in two stages as shown by the patterns revealed on the broken fiber surface. Another type of crack initiation is illustrated by Fig. 6.45. Here the origin of the fracture is in the cortex closer to the center (see the small hole) and the fracture propagates in all directions from this point of origin.

When the hair is dry and between 30% and 90% RH, and slowly extended to break, the step fracture is the primary fracture pattern (Figs. 6.46 and 6.47). For the

Fig. 6.44 Smooth fracture. Note the origin of the crack is in the cortex near the cuticle-cortex boundary (SEM kindly provided by Sigrid Ruetsch)

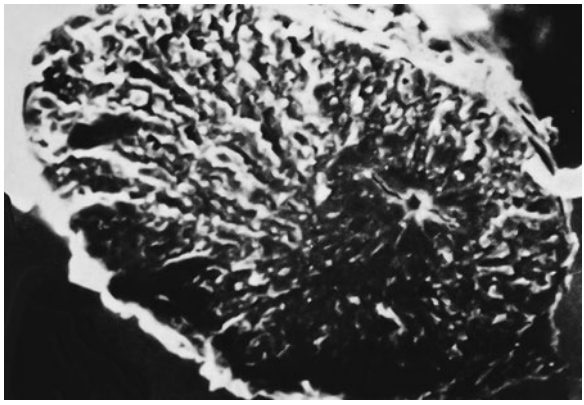


Fig. 6.45 Smooth fracture. Note the origin of the crack is close to the center of the fiber (SEM kindly provided by Sigrid Ruetsch)

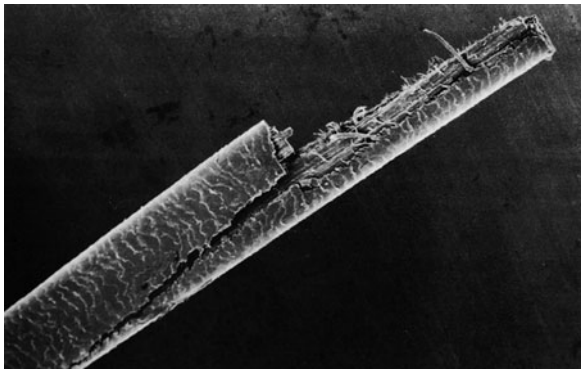


Fig. 6.46 Step fracture. Note the extension of the crack along the fiber length inside the step (SEM kindly provided by Sigrid Ruetsch)

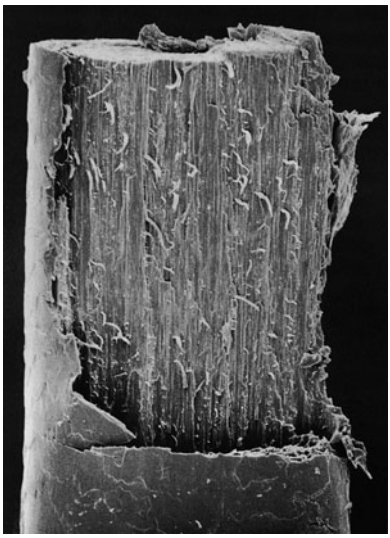


Fig. 6.47 Step fracture (SEM kindly provided by Sigrid Ruetsch)

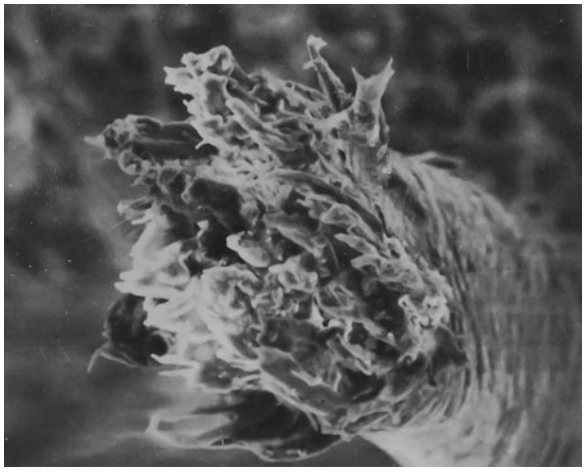


Fig. 6.48 Fibrillated end. Fiber fractured at 65% RJ [166] (Reprinted with permission of the Journal of the Society of Cosmetic Chemists)

fiber depicted in Fig. 6.46, the axial cleavage extends well beyond the step. However, for the fiber illustrated by Fig. 6.47 it stops at the step and moves perpendicular to the fiber axis to terminate. Long single step fractures like these usually originate near the surface. When the fracture reaches a weakness along the axis, e.g., the cell membrane complex (weakened by free radical reactions) or the medulla, it then travels along the axis until it reaches a weakness perpendicular to the axis to break away from the rest of the fiber. Many treatments that damage the cortex cell membrane complex (sunlight, bleaches and certain heat treatments, e.g. free radical reactions) tend to increase the susceptibility of hair to multiple step fractures rather than a single step fracture.

Although fibrillation (Fig. 6.48) and splitting are not the primary fracture patterns, fibrillation and splitting do tend to occur to some degree with more damage or more

twisted or kinky fibers and when the relative humidity is lower, rather than when the fiber is wet. Thus, although fiber breakage by extension does produce different end effects, with rubbing overtime from grooming actions the different fracture patterns can lead to split ends. For more details on split end formation and types see the sections on hair breakage and split ends in Chap. 10.

6.9.4 Damage by Removal of Structural Lipids

The dissolution or the removal of structural lipids or proteinaceous matter from hair, probably from the cell membrane complex or the endocuticle, by either shampoo, by surfactant solutions or by other cosmetic treatments, has been demonstrated by several different scientists. For example, Marshall and Ley [167] demonstrated the extraction of proteinaceous components from the cuticle of wool fiber by surfactant solutions of sodium dodecyl sulfate, cetrimonium bromide and triton X-100. Scott (private communication) showed that part of the lipid components of the cell membrane complex of hair were removed by bleaching while Zahn et al. [35, 168] showed that part of the lipid components of the cell membrane complex were removed by permanent waving.

Zahn et al. [168] determined that intercellular lipids can be extracted from hair during repeated washing with detergents. Gould and Sneath [34] examined root and tip end sections of scalp hair by transmission electron microscopy and observed holes or vacancies in the thin cross-sections. These holes were more frequent and larger in tip ends than in root ends. Gould and Sneath attributed these holes to damaging effects by shampooing, or the breakdown and removal of components of the non-keratin portions of the hair (lipids and proteins) by shampoos leaving the intercellular regions more susceptible to rupture, cracking and fragmentation analogous to permanent waving and bleaching (Ruetsch, private communication). Duvel and Wertz et al. [169] demonstrated that the concentrations of free polar lipids and covalently bound fatty acids decrease from the root end to the tip ends of human hair fibers. In addition, these scientists found a significant reduction in the tensile properties of tip ends versus root ends of hair. Duvel and Wertz et al. concluded that the progressive loss of these structural lipids are likely related to weathering and grooming of hair and they somehow play a role in the decrease in the tensile properties.

To summarize, damage to the non-keratin regions of hair can result from chemical treatment or stretching (cyclic extension or fatiguing actions) or bending of hair fibers creating weaknesses and fractures between the scales other non-keratin regions. This type of damage is more likely to occur in tip sections or in weathered hair than in root ends. Furthermore, research from many different laboratories shows that the action of detergents can lead to or exacerbate this type of damage by chemically/physically breaking down and partially dissolving non-keratin matter from the hair. This type of damage is more likely to occur on hair where the cell membrane complex has been damaged by oxidative treatments or weathering actions or by reduction, than on undamaged root sections of hair. Furthermore, treatment of hair containing weakened

a weakened cell membrane complex containing penetrated ingredients can either accelerate or retard cuticle fragmentation.

Thus, it is becoming increasingly clear that shampooing and rubbing actions such as those that occur during grooming over time actually does damage hair by abrasion/erosion/dissolution actions. In addition, stretching or bending of hairs when a snag is encountered (cyclic extension/bending or fatiguing-like action) also produces weaknesses or cracks in the non-keratin regions of the cuticle. Similarly the rapid loss of heat as in heat drying can also produce cracks in surface cuticle layers especially when hair is deformed during heating as in blow drying and combing or with curling irons. These actions lead to scale lifting and produce even further damage by rendering those areas more susceptible to cuticle fragmentation and to the penetration of chemicals into the hair. This latter effect occurs because the non-keratin regions are areas of entry for penetration into the fiber. Furthermore, weakening of the non-keratin or cell membrane complex regions by either stretching, bending or by penetrating chemicals or sunlight will ultimately lead to the degradation of the cortex in addition to the cuticle and to an even faster rate of penetration of damaging treatments into the hair.

Thus, without question, normal cleaning and grooming practices that involve washing hair with simple shampoos or even with soap ultimately contributes to cuticle and even to cortical damage by abrasive/erosion and cyclic bending and extension actions and by the dissolution of components from the non-keratin regions of the fiber. These damaging effects are ultimately detected by consumers as dry and dull ends or as brittle hair and split ends and by an increased sensitivity of their hair to rubbing actions during grooming and to other damaging cosmetic treatments. In addition, Tolgyesi [170] has shown that sunlight and chemical processing treatments such as bleaches, permanent waves, straighteners, and some hair dyes or even chlorinated water from swimming pools can accelerate these damaging actions to the hair by making the hair even more susceptible to chemical and physical damage.

One fascinating observation is that this type of damage is detected most readily by microscopic techniques or macro detection techniques. It seems to me that the development of methods to measure swelling of the upper cuticle layers or other sensitive means to detect cuticle damage may someday reveal this damage in a more sensitive manner than the techniques used today. For a crack to appear in the hair, considerable damage at the molecular level and higher levels must have occurred, leaving room for detection to a more sensitive degree than by the methods being used today.

The best technique to monitor hair breakage and thus hair strength is to actually comb the hair and measure the amount of hair broken off. Other techniques not commonly used such as extension cycling, and rubbing fibers to break are in this author's opinion more relevant to hair damage and hair breakage than tensile testing. This is because extension cycling and rubbing actions more closely simulate combing and brushing of hair than the very slow strain rates and the high percentage extensions generally employed in tensile testing. For a more detailed discussion of this subject, see Chap. 10.

6.10 Hair Breakage by Grooming Actions

Hair breakage during combing and brushing is covered in detail in Chap. 10 in the section entitled, *Breakage of Hair during Grooming Actions*, see Refs. [165–177] and the references in Chap. 10 on this subject.

6.11 Dandruff, Scalp Flaking and Scalp Care

Dandruff results from a scalp malfunction and is not directly related to the chemistry and physics of human scalp hair. However, antidandruff products must be compatible with other hair products, and they have become an increasingly important hair care category over the past several decades. Therefore, the subject of dandruff and antidandruff active ingredients merits some mention in a book dedicated to the chemistry and physics of human scalp hair. Antidandruff products are the most prevalent scalp care product, although claims beyond dandruff such as anti-seborrheic, dry scalp care and eczema treatment are made for some of these. This section attempts to provide an entry into the literature relevant to scalp care products.

The relatively recent review by Pierard-Franchimont, Xhauflaire-Uheda and Pierard [178], with a few other sources has been relied upon for updating this section on dandruff. Dandruff (seborrhea sicca, pityriasis sicca, or sicca capitis) has been defined by Kligman as "chronic noninflammatory scaling of the scalp" [179], as observed clinically. This definition allows clinicians to differentiate between dandruff and other scaly scalp diseases such as psoriasis, atopic dermatitis or seborrheic dermatitis, etc. Others have demonstrated histologically that inflammation exists in the upper dermis in dandruff [180]. Furthermore, it is clear that inflammation is critical to the development and to the treatment of dandruff. Nevertheless, these facts do not negate or reduce the utility of Kligman's definition of dandruff for clinical evaluation.

The stratum corneum in the dandruff scalp is thinner [181] than in the normal scalp. In addition, the epidermal turnover rate is increased in dandruff [181, 182]. It has been suggested that this rapid transfer of cells to the scalp surface inhibits complete keratinization of the stratum corneum. Therefore, the developing stratum corneum becomes less coherent, cracks develop, and flakes result. Market research shows that 80–90% of adults suffer from some form of scalp flaking problem. About 40% of these have dry scalp and 30–35% have dandruff. But, Robert Walther of New York Presbyterian Hospital estimates that only 4–5% of those with a scalp problem go to a physician. Thus, most of these consumers either conclude that they have dandruff or they deny any scalp malfunction.

Dandruff is age-related [183], rarely seen before puberty, but common with the onset of puberty. It peaks in the early twenties and declines in middle and further

advancing age. Dandruff appears to be seasonal, being most severe in the winter months (October through December) and milder in the summer [183]. Dandruff occurs equally among males and females [184]. The primary cause of dandruff today is believed to be the Malassezia spp. Flora [178]. Decades ago lipophilic yeasts of the genus Malassezia, previously known as Pityrosporum, were believed to be the primary cause of dandruff [185, 186]. In the 1960s and 1970s this fungal relationship was widely disputed [187]. However, after decades of additional research most today agree that the primary cause is Malassezia spp. Flora. It is also accepted that some auxiliary non-microbial causes are also operative such as various types of irritants [178].

6.11.1 The Cause of Dandruff

Ive [184] suggested that high levels of sweat and sebum production and the use of alkaline soaps are "predisposing factors" for the disease spectrum of dandruff/seborrheic dermatitis. Years ago, Van Abbe and Dean [186] suggested that dandruff is an adaptive response to a threshold irritation. The irritation could result from metabolic products of Malassezia, from other microflora, or other sources. This conclusion is consistent with the observation of Heilengotter and Braun-Falco [180] that inflammation can be detected histologically in dandruff. Some experts [184] say that mild seborrheic dermatitis and psoriasis have features indistinguishable from dandruff. In more severe cases, psoriasis (Fig. 6.49) can be distinguished from dandruff (Fig. 6.50). In milder cases of seborrheic dermatitis and dandruff, distinctions made readily by clinicians or dermatologists are not easily made by untrained consumers who generally do not go to a physician for diagnosis. In fact most consumers who exhibit the combined symptoms of scalp flaking and itching, of almost any origin, call their condition dandruff.

Dandruff clinicals today are generally conducted in temperate climates, in the "winter time", during the "dandruff season". Yet, scalp flaking and itching does occur in tropical and subtropical climates and dandruff does exist for some even in the summer. Most consumers who exhibit these symptoms in any climate call their condition dandruff. The data of Table 6.22 show that the Malassezia activity of

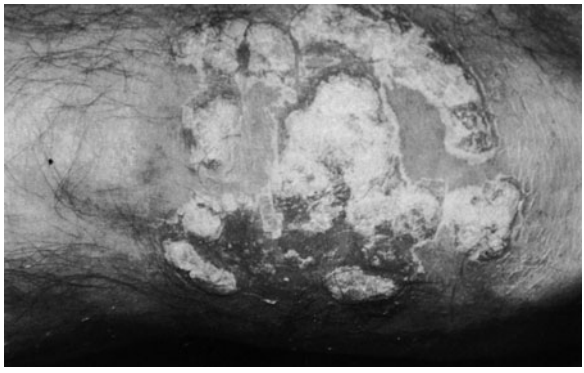


Fig. 6.49 Photograph illustrating the silvery scaly condition of psoriasis

Fig. 6.50 The dandruff scalp; note the small dry scaly dandruff flakes

Table 6.22 Dandruff actives and Malassezia activity (minimum inhibitory concentration [MIC])

Active ingredient	MIC versus Malassezia	% Active shown Effective versus dandruff	Suggested mechanism
Sulfur	50	2–5[a]	–
Selenium sulfide	2,000	1[a]	Cytostatic
Coal tar	2,000	0.5–5[a]	Cytostatic Anti-inflammatory
Salicylic acid	100	1–2[a]	Keratolytic
Zinc pyrithione	1	1–2[a]	Antifungal
Climbasole	1	0.5–2	Antifungal
Ketoconazole	0.125	1–2	Antifungal

[a]Percent concentrations shown effective against dandruff

several common antidandruff agents varies by 4 orders of magnitude and that coal tar, although effective against dandruff, has virtually no activity against Malassezia yeasts.

Furthermore, selenium sulfide exhibits substantially lower activity against Malassezia than ketoconazole, however, in 4 out of 5 clinical studies, these two antidandruff agents were found to be equally effective against dandruff. Ketoconazole was shown to be more effective in only 1 of the 5 studies [188]. Ketoconazole has also been shown by Pierard et al. [189] to inhibit Malassezia growth on the scalp and the hair for longer periods of time than zinc pyrithione or selenium sulfide. If Malassezia is the primary cause of dandruff and ketoconazole is orders of

magnitude more effective against this fungus, then other variables must be involved to help explain the reason why it is not more effective than the other agents in clinical testing. Variables such as the affinity of Malassezia to specific corneocytes, or the presence of certain irritants or antiirritants in formulations have been cited as possibilities [178].

We have been able to generate the symptoms of scalp flaking and itching with mild erythema by daily treatment of panelists with a shampoo in warm weather clinical conditions. These panelists called their condition "dandruff". Further, we were able to demonstrate that this condition could be improved by either the same shampoo with climbasole (antifungal and anti-inflammatory agent) or by treatment with a shampoo containing aspirin (anti-inflammatory agent) versus a placebo shampoo. Aspirin exhibits virtually no microbiological activity against Malassezia.

The results of this study are consistent with Van Abbe's original hypothesis that dandruff is an adaptive response to a threshold irritation. Our conclusion is that dandruff, diagnosed by consumers, is an inflammatory disease with multiple causes (irritants). The primary cause for the production or appearance of irritants is Malassezia spp., however, consumers susceptible to harsh detergents or alkaline soaps or to metabolic irritants produced by Malassezia respond when exposed to these irritants and produce the symptoms of scalp itching and flaking and call their condition dandruff. The cures are to either eliminate the primary irritant cause by antifungal agents and/or to combat the symptoms with an anti-inflammatory agent such as aspirin, steroids or antidandruff agents that contain anti-inflammatory properties.

As is frequently the case, if the irritant is produced by Malassezia then an antifungal agent is effective. However, if the irritant is alkaline soap or a harsh shampoo, as in the warm weather clinical above, elimination of the irritant and treatment with an anti-inflammatory is the remedy of choice. Many common antidandruff agents also exhibit anti-inflammatory behavior, for example, climbasole, zinc pyrithione and ketoconazole known as antifungal agents are also anti-inflammatories and can function to improve the scalp condition to some degree even when Malassezia is not the primary causative agent.

Another interesting characteristic of antidandruff shampoos is their effect on sebum. For example, selenium disulfide in a shampoo increases sebum production [190, 191] and it alters the ratio of triglycerides to free fatty acids found in sebum. Presumably, this latter effect involves reducing the microflora responsible for producing lipolytic enzymes on the scalp that hydrolyze triglycerides to free fatty acids. Zinc pyrithione appears to behave similarly and has been shown to increase hair greasiness [19], presumably in an analogous manner. However, ketoconazole behaves in the opposite manner. Pierard-Franchimont et al. [53] confirmed the increase in sebum excretion rate for selenium sulfide and further demonstrated that ketoconazole decreases sebum excretion. The effects of most antidandruff agents to increase sebum levels in hair are analogous to the effects on sebum production during puberty [192] and opposite to the effects on sebum production in post-menopausal women [193], see Chap. 1 for more details.

6.11.2 Antidandruff Treatments and Hair Shedding (Telogen Effluvium)

In some cases, hair shedding and hair thinning have been associated with dandruff and seborrheic dermatitis. Pierard-Franchimont et al. [194] conducted a study among 150 men selected to have abnormal shedding of hair related to androgenetic alopecia associated with dandruff. This panel was separated into three different groups and treated with shampoos containing either 1% ketoconazone, 1% piroctone olamine or 1% zinc pyrithione. Each group was instructed to shampoo 2–3 times a week for 6 months. Hair shedding during shampooing, hair density on the vertex, anagen percentages, hair shaft diameters, itching (pruritus) and dandruff were evaluated in all three groups. The results showed that hair shedding decreased from all three treatments. The anagen percentage also increased for all three treatments, but the hair shaft diameter increased only for the ketoconazole and piroctone olamine treatments. Hair shaft diameter did not increase for the zinc pyrithione treatment. A primary conclusion was that telogen effluvium or abnormal shedding of hair associated with dandruff was controlled by all three antidandruff shampoos.

6.11.3 Antidandruff Ingredients and the Evaluation of Dandruff

The OTC monograph of 1983 recommended three classes of potential antidandruff ingredients [183]:

Category I: Active ingredients considered safe and effective for use for dandruff, seborrheic dermatitis and psoriasis.
Category II: Ingredients not recognized as safe and effective or misbranded.
Category III: More data are required.

Actually, at this time only two categories are recognized: Category I, as defined above, and Category II. All other ingredients are not recognized as safe and/or effective in this more recent classification.

Six ingredients are currently recognized as safe and effective for use against dandruff in the United States, and these are listed in Table 6.23. The OTC recommends each ingredient at specific concentrations for specified purposes (products and applications). Other ingredients either reported or shown to be effective against dandruff and described either in the OTC monograph, the published literature, or the patent literature include alkyl isoquinolinium bromide, allantoin, benzethonium chloride, magnesium omadine, climbazole (1-Imidazopyl-1-(p-chlorophenoxy)-3,3-dimethyl butan-2-one), and octopirox (1-hydroxy-4-methyl-6-(2,4,4 trimethyl pentyl))-2 (1H) pyridine ethanolamine. These latter ingredients have not been described in category I by the OTC monograph, however,

Table 6.23 Active ingredients for dandruff

Ingredient	Concentration (%)	Use
Coal tar preparations	0.5–5.0	Shampoos
Salicylic acid	1.8–3.0	Body and scalp products
Selenium sulfide	1	Topical use
Sulfur	2.0–5.0	Topical use
Zinc pyrithione	1.0–2.0	Shampoos
	0.1–0.25	Hair groomers
Ketoconazole	1–2	Shampoos

they are highly effective against dandruff and climbasole is widely used outside the United States.

Several methods have been described to evaluate dandruff, such as brushing off the hair and/or the scalp with various devices and weighing the scruf [182, 195]. However, the most popular approach involves partitioning the scalp into several areas, rating each area for dandruff severity, and analyzing the combined data statistically [196]. The scalp partitioning method using appropriate statistical procedures provides a powerful tool to evaluate dandruff severity and the efficacy of antidandruff products.

6.11.4 Effect of Medium (Delivery) on Antidandruff Efficacy

A study by Georgalas [197] demonstrated that Octopirox at 0.2% in 10.5% sodium laureth sulfate plus 3% sodium lauroyl lactylate was more effective than the same active ingredient at 0.2% in 10.5% sodium laureth sulfate (with no lactylate) and just as effective as octopirox at 0.5% in 10.5% sodium laureth sulfate (with no lactylate). This effect was explained by an enhanced delivery of the active antidandruff agent to the hair and the scalp in the mixed surfactant system. The authors suggested that acyl lactylates have demonstrated spontaneous formation of vesicles and solubilization of the active ingredient.

6.11.5 Effect of Residence Time on Antidandruff Efficacy

Pierard-Franchimont et al. [198] determined that a 5 min residence time improves antidandruff efficacy for both 1% ketoconazole and 1% piroctone olamine containing shampoos. Both shampoos showed improvements in scaliness and yeast colonization. However the increased treatment time provided more improvement to the piroctone oleamine treatment than for the ketoconazole containing shampoo.

6.12 Toxicity, Regulation, Product Safety and Skin Irritation

6.12.1 Regulation and Safety Issues (USA)

Several toxicity, irritation and sensitization phenomena will be summarized in this section with special reference to hair care products that contain surface active agents. Skin irritation by surfactants will be covered in some depth providing a few fundamental principles and useful relationships of skin irritation to surfactant molecular structure to provide guidance for formulating milder hair care products. But first, a few important regulatory statutes will be summarized and referenced for further follow up as needed.

The Food, Drug and Cosmetic Act of 1938 provided definitions for cosmetics and drugs and prohibited interstate commerce for cosmetics that are adultered or misbranded. By definition, adultered means that the product, contains a poisonous or deleterious substance, a non-permitted color additive or filthy, putrid or decomposed substance or it was manufactured or held under non-sanitary conditions. Misbranded means it contains false labeling, does not contain the required labeling or it is not truthfully packaged.

By this act, cosmetics are "those articles (or their ingredients) that are applied to the human body for cleansing, beautifying, promoting attractiveness, or altering the appearance without affecting the body's structure or function." On the other hand, "those articles promoted as cosmetics, but also intended to treat or prevent disease or to affect the structure or functions of the human body are drugs as well as cosmetics and must comply with the requirements for both drugs and cosmetics." By these definitions, an antidandruff shampoo is an over the counter (OTC) drug and cosmetic while a cleaning or conditioning shampoo is a cosmetic. Soap bars are exempt, that is, are not restricted by regulations of either cosmetics or drugs.

The Federal Hazardous Substances Acts (FHSA) of 1940 and of 1960 defines five areas of acute toxicity/irritation that are of primary importance for the development and sale of consumer products: acute oral toxicity, dermal toxicity, primary dermal irritation, eye irritation, and acute inhalation toxicity. The FHSA act describes recommended test conditions in detail for these toxicity/irritation phenomena. Some knowledge of the potential for sensitization and phototoxicity are also relevant. It is also necessary to provide long term safety assurance related to potential carcinogenicity and mutagenicity.

Carcinogens react with nuclear material to alter the feedback mechanism that normally limits cell replication. Carcinogenicity and long term safety are not the objective of this section. Other sources should be consulted to properly cover these subjects. In the mid-1960s the FDA set up an expert panel to review OTC drug ingredients. This group initially proposed three categories from the perspective of safety and efficacy. The three categories are: Category I (safe and effective), Category II: (not safe or effective) and Category III (more data is necessary for a decision). In the 1980s group III was eliminated. Over the years, OTC panels have met to classify several types of ingredients in these categories to provide safety and

efficacy guidance for OTC products. In the section on dandruff products, results of the OTC panel on antidandruff ingredients are described.

The Toxic Substances Control Act of 1977 (TSCA), written October 11, 1976 but became effective January 1, 1977 and was enacted to control new ingredients. It stated that any ingredient sold, manufactured, imported or processed for use in a consumer product must be on the TSCA inventory. This process required, filing a pre manufacturing notification (PMN) with the Environmental and Protection Agency (EPA). The PMN must contain safety data to demonstrate the ingredient to be safe within reasonable doubt. The EPA must reply within 90 days to list the ingredient or recommend additional testing [199]. EINICS is the European equivalent to TSCA and it controls the registration of new ingredients sold in consumer products in Europe. Many other countries have their own equivalent to TSCA to regulate the use of new ingredients sold in consumer products.

One principle that has become increasingly relevant to all of these phenomena is the existence of a threshold effect. The threshold effect means that below a specific concentration, for each ingredient and each phenomenon, there will be no irritation, sensitization or toxicity. This principle is especially important to products when impurities, fragrance components and preservatives are being questioned, that is, where exceedingly low levels of ingredients are involved. The reason is that many sensitizers are capable of causing reaction at or below 0.5% concentration (but not at part per million levels) while potential carcinogens can be active at even lower concentrations.

The existence of a threshold effect in sensitization and long term toxicity was open to question only a few decades ago. However for sensitization and skin irritation a threshold effect is clearly accepted today. Decades ago, the Delaney Clause in the Food Additives Amendment of 1958 to the Federal Food, Drug and Cosmetic Act called for “absolute safety”, that is, the elimination of color additives containing a carcinogenic “constituent”. However, in the 1980s the FDA took action that allowed for approval of color additives containing a carcinogenic “constituent”, if it could be shown that the additive was safe under conditions of use. This FDA action provides indirect recognition of a threshold effect in carcinogenicity and in long term toxicity.

6.12.2 Eye Irritation

For testing new ingredients or new products, separate and distinctly different tests are used to assess potential eye and skin irritation. That’s because these two phenomena are different mechanistically. Nevertheless, as a first approximation, most materials that are irritating to skin are also irritating to eyes and vice versa.

The Draize rabbit eye irritation test has been used for decades as an animal model to predict eye irritation in humans. However, since the rabbit eye does not tear, and of course the human eye does, this model is imperfect for predicting irritation to human eyes. Obviously, the rabbit eye test cannot be used to evaluate

Table 6.24 Effect of ethoxylation on skin and eye irritation by anionic surfactants

Surfactant (no. EO units)	Concentration (%)	Eye irritation score[a]	Skin irritation rank[b]
Sodium lauryl sulfate@[0EO]	21	295	I
TEALS [0EO]	21	224	I
TEALS [0EO]	25	240	
TEALS [0EO]	30	295	
Sodium laureth-1sulfate [1EO]	21	487	
Sodium laureth-2 sulfate [2EO]	21	511	II
Sodium laureth-3 sulfate [3EO]	21	406	II
Sodium laureth-6 sulfate [6EO]	21	63	IV
Sodium laureth-12 sulfate [12 EO]	21	37	IV

[a]Totals scores of conjunctivitis, iritis and corneal irritation in Draize eye test. The totals generally agree with the most severe eye damage

[b]Ten percent solutions of the detergents were applied to humans by washing two times daily on the ante-cubital spaces of test subjects and then rinsing. Each day the subject's skin was scored for irritation and the surfactants separated into four groups based on their relative irritation ranks. The most irritating group was labeled I and the least irritating IV

"no more tears" shampoo claims. A large number of laboratory models have been examined over the past decade to provide a predictive tool to be used either in place of or to minimize the use of animals for eye testing. Among these models, the HET-CAM test and the CAM-VA assay by Spielmann et al. [200] show promise.

As indicated above, those materials that are skin irritants are oftentimes eye irritants too, although there is not a perfect correlation between the two tests. The data of Table 6.24 show that adding up to 12 ethylene oxide units to an alcohol sulfate detergent as sodium laureth-12 sulfate produce virtually no skin irritation. However, adding only 1–3 ethylene oxide units creates sodium laureth-(1–3) sulfate a surfactant that is more irritating to eyes, but further increasing the number of ethoxy groups beyond 3–12 decreases both eye and skin irritation.

6.12.3 Skin Irritation

The irritation of human skin can be considered as a four step process. The potential irritant must first adsorb to the stratum corneum, the outer protective "non-living" barrier membrane, see the schematic of Fig. 6.51. The next step involves diffusion through the non-living stratum corneum. The substance can disrupt the stratum corneum and/or desorb into the living tissue where it can react to cause the symptoms of irritation.

When an irritating ingredient reacts in the living tissue (the epidermis), histamine, a natural vasodilator is released. Histamine increases the blood flow (fluid) into the irritated site. Fibinogen, a clotting protein causes a "walling off" in the tissue to prevent the spread of the toxin or irritant. These defensive reactions help to account for the clinical symptoms of redness and swelling that are frequently

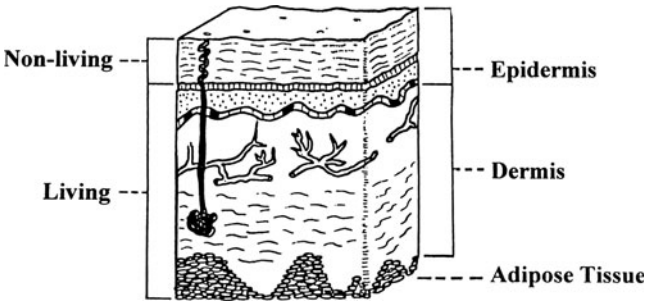


Fig. 6.51 Schematic diagram illustrating a section of human skin. Note the non-living barrier membrane called the stratum corneum

associated with irritation. Dryness and scaling or flaking of skin result primarily from reactions in the stratum corneum itself, although reaction in the living layers immediately beneath the stratum corneum can also lead to flaking of skin by increasing the turnover time, analogous to flaking of the scalp associated with dandruff.

The types of tests used to assess skin irritation potential of ingredients or products are many and are varied. Tests on animals of different species are used to assess safety and are usually blunt tools. Rabbits, guinea pigs and humans are frequently used species. Human in-vivo tests of products or solutions of ingredients applied under patches or in plastic or glass chambers have been used. Arm or hand immersion or repeat applications to sensitive areas, such as the inside of the forearms or the cheeks are also common test sites.

Many in-vitro models have also been developed to assess skin irritation. Many of these involve the swelling of human or animal skin by Robbins and Fernee [110], the swelling of a collagen film by Blake-Haskins et al. [201], water vapor loss by Van der Volk [202] and squamometry by Paye and Cartiaux [203]. All of these methods have shown some degree of correlation to skin irritation on humans and animals. The results from many of these tests have been considered in the next section to provide some "rules of thumb" to describe and compare the relationships of skin irritation potential for various surfactants.

A mathematical model will also be presented to allow prediction of the relative irritation potential of mixtures of surfactants, that is, of products such as shampoos and light duty liquid detergents.

6.12.4 Principles for the Relative Skin Irritation by Surfactants

The following five "rules of thumb" for skin irritation by surfactants are followed with only a few exceptions. These rules can facilitate in developing surfactant products that are mild to skin.

1. For each type of surfactant, there is generally a maximum in skin irritation that usually occurs at a chain length of 12 carbon atoms on the hydrophobic part of the surfactant molecule.
2. Adding or increasing the number of ethylene oxide units in a surfactant usually makes it milder to skin.
3. There is a good correlation between increasing the molecular weight of an anionic surfactant and mildness to skin. This rule probably applies to all surfactants at the peak irritation structure of 12 carbon atoms, but not below.
4. Molecular association between different surfactants makes the ingredients (system) milder to skin, for example, adding cationic or amphoteric surfactants to anionic surfactants decreases the irritation by the anionic.
5. It is possible to describe the relative irritation potential for mixtures of surfactants (products) by a mathematical model involving linear combinations of irritation constants for each surfactant multiplied by its concentration.

The remaining part of this section on skin irritation is concerned with describing these five principles of surfactant mildness in more detail.

6.12.5 Support for the Principles of Surfactant Skin Irritation

6.12.5.1 Anionic Surfactants

From a synthesis of the results in the literature describing in-vitro and in-vivo skin irritation, for most anionic surfactants regardless of the hydrophilic group, there is generally a maximum in skin irritation at a hydrophobic chain length of 12–14 carbon atoms. For example, consider alkyl sulfates. For the swelling of human epidermal membrane by Robbins and Fernee [110] and for irritation of human skin by Kligman [204], there is a maximum at 12 carbon atoms, see Fig. 6.52. For alkyl benzene sulfonates and for alpha olefin sulfonates, Imokawa et al. [205] have shown a maximum in the generation of skin roughness at 12 carbon atoms and for sodium salts of fatty acids, Matthies [206] has described a maximum in skin irritation at 12 carbon atoms.

Alkyl ether sulfates of dodecyl sulfate show a decrease in skin irritation and skin swelling [204] with increasing ethoxy numbers from 1 to between 9 and 12 units of ethylene oxide where the irritation is negligible, see Table 6.24.

6.12.5.2 Nonionic Surfactants

Although nonionic surfactants are generally less irritating to skin than analogous anionic and cationic surfactants, neat solutions or high concentrations of some ethoxylates can produce severe irritation, see the data of Table 6.25. These data show that the effect of increasing ethylene oxide units produces less irritation,

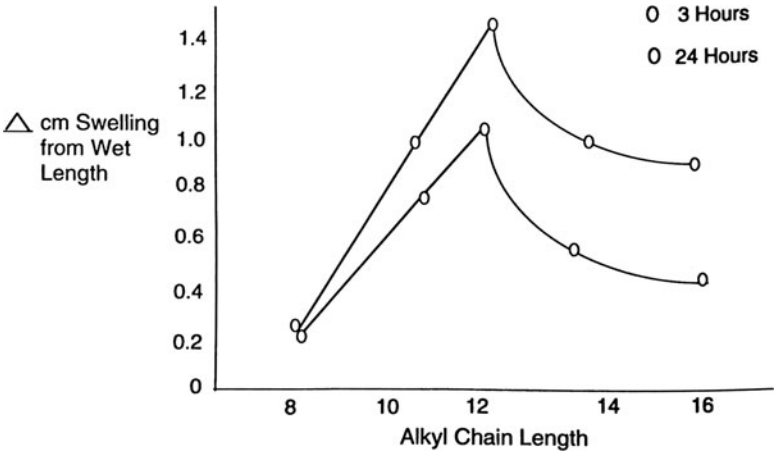


Fig. 6.52 Chain length of alkyl sulfates and skin swelling. Note the peak in swelling at an alkyl chain length of 12 carbon atoms [110] (Reprinted with permission of the Journal of the Society of Cosmetic Chemists)

Table 6.25 Skin irritation in rabbits by nonionic surfactants [207]

Surfactant	Irritation score[a]
C9-11-2.5 EO	Extreme (7.75)
C12-15-7 EO	Severe
C14-15-7 EO	Severe
C14-15-11 EO	Moderate
C14-15-13 EO	Moderate (3.59)

[a]Twenty-four hours on rabbits backs occluded patch 100% concentration. Max score 8.0

similar to that of increasing the chain length of anionic surfactants. A maximum in irritation at 12 carbon atoms is not shown by these data, probably because of the limited chain length variation in the nonionics tested.

With nonionics containing only a few ethylene oxide groups, another concern is that some of these such as laureth-3 can anesthetize eyes. This effect poses a problem in a shampoo type product formulated with irritating surfactants; however, fortunately these surfactants are not normally used in shampoos.

6.12.5.3 Amphoterics and Cationics

Solutions or dispersions of amphoteric and cationic type surfactants were tested at 10% concentration on humans along with several other types of surfactants by washing two times daily on the antecubital spaces of test subjects and then rinsing. Each day the subjects' skin was scored for irritation and afterwards the surfactants were separated into four groups based on their relative irritation rankings. The most irritating group included cocamine oxide and coco-betaine which were in the same

group as sodium lauryl sulfate. On the other hand, cocamidopropylamine oxide was in the second most irritating group as was sodium cocoamphoacetate. A cationic polymer (polyquaternium-7) and steartrimonium chloride were in the least irritating group.

The results of these tests show decreasing irritation with increasing molecular weight and are consistent with a maximum in irritation at 12 carbon atoms for the hydrophobe, since the coco hydrophobe is 50% C 12. Amphoteric surfactants are generally perceived to be mild to skin, because they function as anti-irritants in the presence of anionics. However, the above data for amphoteric structures alone in the absence of anionics shows that these surfactants can be irritating to skin.

The anti-irritant effect produced by amphoteric surfactants is caused by molecular association. The irritating species in a surfactant system is the surfactant monomer, not larger associated species such as aggregates. One of the effects of amphoterics and amine oxides in the presence of anionics is to associate with the anionic resulting in a lower monomer concentration. Furthermore, the associated species is larger and less irritating than surfactant monomer. Interestingly, today we view amphoteric surfactants as mild and as anti-irritants because they are generally used in the presence of large amounts of anionic surfactants. If we formulated differently with an excess of amphoteric, then we would view anionics such as sodium lauryl sulfate as anti-irritants and amphoterics as the irritating species.

We usually associate anti-irritation with amphoteric surfactants; however, since other types of surfactants, such as glucamide or alkyl poly glucoside (APG), perform this function and these are structurally not amphoterics or cationics, I would suggest that we call this type of surfactant a “pseudo-amphoteric” surfactant. Furthermore, I would propose that we promote the concept of classifying surfactants on the basis of their function rather than their structure. More on this subject will be presented in the following sections.

Most of the cationic surfactants that are used as conditioners in hair care products are high molecular weight species similar to steartrimonium chloride or polyquaternium-7 and are used at low concentrations generally below the threshold for irritation.

6.12.5.4 Molecular Weight (Size) and Skin Irritation

During the course of our studies on skin irritation by surfactants, we made the observation that there appeared to be a correlation in skin swelling with molecular weight of surfactants. The plot of Fig. 6.53 summarizes our data on skin swelling and molecular weight for 27 different anionic surfactants. These data show a significant inverse relationship between surfactant molecular weight and skin swelling. The index of determination for this quadratic model is 0.7 suggesting that 70% of the variation in skin swelling is explained by the variation in molecular weight. Since four surfactants tested here had hydrophobic chain lengths below C12, an even greater molecular weight influence exists above that lower limit.

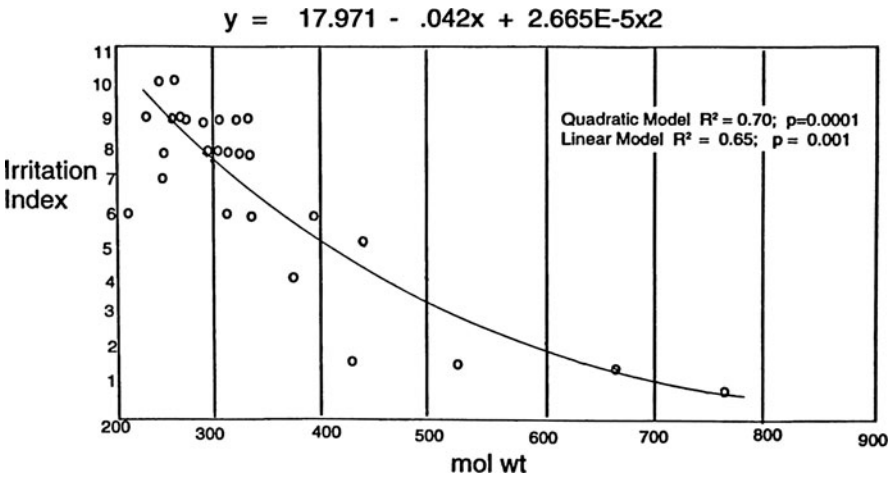


Fig. 6.53 Skin irritation and molecular weight of anionic surfactants. Note the decrease in irritation with increasing molecular weight (size)

Although we have not tested this effect for other types of surfactants, it is clear that molecular weight (as a rough approximation to molecular size) does explain a large part of skin swelling and since skin swelling correlates with skin irritation by surfactants; molecular weight must explain a large part of skin irritation. This is because the larger the size of the molecule, the slower its penetration across the stratum corneum into the living tissue and thus the less irritation produced. About 30% of the variance is due to other factors, such as molecular shape and the hydrophilic functional group.

6.12.5.5 Mathematical Model to Predict Skin Irritation

The relationship observed for the swelling of stratum corneum and skin irritation and the existence of a large amount of data on skin swelling provided encouragement to explore the possibility of a mathematical model to predict skin irritation of mixed surfactant systems or products based on skin swelling data.

The first step was to develop irritation constants for a large number of individual surfactants. Crosswise swelling data conducted with rectangular pieces of human stratum corneum on individual surfactants after soaking the skin in 1% sample solutions at 40°C for 1,6 and 24 h were employed. Average swelling ratios were normalized to a scale of 1.263 for sodium lauryl sulfate and 1.00 for water forming the original scale. Normalization was necessary to compensate for variation between different skin samples used, for the large number of surfactants employed. At first, normalized swelling values were only assumed to reflect irritation indices, however, later swelling values were shown to correlate with skin irritation rankings

from in-vivo testing on humans by Spearmans Rank Correlation method, see Table 6.26.

Additional irritation indices were determined for anionic and neutral surfactants until data from more than 20 different surfactants had been collected. For cationic and amphoteric surfactants, negative irritation indices were initially assigned a value of −10 (see Table 6.27). Later, charge density was used to more accurately estimate irritation indices of counter irritants assuming stoichiometric interaction between anionic and cationic or amphoteric detergents. With additional testing, a few surfactants such as APG, Monamate CPA-40 and Glucamide were found to interact with anionic surfactants producing a mildness response and appropriate irritation indices had to be estimated for these, "pseudo-amphoteric" detergents.

Although, several in-vitro methods have been used quite extensively to predict irritation by products and individual surfactants, it is known that magnesium ion can produce false mildness readings by many of these methods. Thus, the advantage of the calculation procedure that can be used to provide a more realistic prediction when flaws of other methods provide false readings such as for pH extremes and the use of divalent ions, at high concentrations, in the presence of anionic surfactants.

To calculate relative irritation for products, simply take the sum of the irritation index of each surfactant multiplied by its concentration (weight concentration) in the product. Then multiply this sum by a normalization factor to place it on a scale between two known extremes in irritation for that product type. An example for shampoos is provided in Table 6.28 to illustrate this approach.

The data of Table 6.28 show a significant relationship between in-vivo irritation and calculated irritation scores. To calculate the irritation, all components at

Table 6.26 Irritation indices from swelling data and in-vivo irritation

Medium/surfactant	Irritation index	Normalized swelling ratio	In-vivo irritation rank
Water	0	1.00	–
Cocamide DEA	2	1.019	1
Sodium laureth-3 sulfate	6	1.067	2
Sodium laureth-2 sulfate	8	1.146	3
Sodium dodecylbenzene sulfonate	9	1.188	4
Sodium lauryl sulfate	10	1.263	5

Table 6.27 Irritation indices for a shampoo with amphoteric surfactants

Surfactant	Irritation index
SLS or ALS	10
CDEA or CMEA	2
SLES-2	8
CAPB or lauroamphoglycinate	−10[a]
Dimethicone or 20–40 alcohols	1

[a]Varies with anionics used (see text)

Table 6.28 Calculation of potential irritation by shampoos[a]

Shampoo type[a]	Calculated irritation	Calculated rank	Actual irritation rank[b]
I baby type	0.28	5	5
II. 2 in 1 A	2.22	1	1
III	0.86	4	4
IV. 2 in 1 B	1.16	3	3
V	1.72	2	2

Shampoo I
14% PEG-20 sorbitan laurate
5% sodium trideceth-3 sulfate
5% lauroamphoglycinate
0.75% glycerine
Colors, preservative and fragrance

Shampoo II
21% ammonium lauryl sulfate
4% cocamideDEA
2% 20–40 alcohols
2% dimethicone
Colors, preservative and fragrance

Shampoo III
10% ammonium lauryl sulfate
3% cocamide DEA
2% cocamidopropylbetaine
Colors, preservative and fragrance

Shampoo IV
14% ammonium laureth-2 sulfate
4% sodium lauryl sulfate
4% cocamidopropylbetaine
2% cocamide MEA colors, preservative and fragrance

Shampoo V
12% ammonium lauryl sulfate
6% sodium laureth-2 sulfate
2.5% dimethicone
2% cocamideMEA
Xanthan gum
Colors, preservative and fragrance

[a]The shampoo compositions used in these calculations are described below
[b]Rank from testing under Duhring chambers using 25% shampoo solutions. Spearman's rank correlation test provides a correlation coefficient of 1.0 and a Z value of 2.0 indicating a significant relationship between in-vivo irritation and calculated ranks

concentrations of 1% or less are deleted unless they are cationics or amphoterics. Similar calculations have been shown to be feasible for light duty liquid dish detergents and for bar products.

The assumption of complete inhibition of irritation of anionics by amphoterics and cationics is obviously not valid, but for the most part this assumption does not provide serious errors in calculation. Recently, we found that several neutral molecules such as APG and glucamide possess anti-irritant properties (although not to the same extent as amphoterics) and it is highly likely that other non-amphoterics behave similarly. To refine these calculations further, more appropriate irritation indices for all anti-irritants should be determined empirically.

6.12.6 Sensitization and Phototoxicity

Sensitization involves allergic reactions of the immune system. Sensitization is a three step process with an initial exposure followed by an induction period that involves the development of antibodies or lymphocytes in response to an antigen.

The induction period usually does not produce symptoms. The third step is called the challenge or elicitation reaction which occurs on subsequent treatments or exposures. Clinically, elicitation occurs about 2 weeks (10 days to 3 weeks) after induction. At this stage, an inflammatory response usually occurs, but if the "walling off" process is not effective, more severe symptoms result.

In hair products, some ingredients known to be capable of producing sensitization reactions are a few fragrance ingredients, formaldehyde and parabens (preservatives), and some hair dye components, such as p-phenylenediamine as shown by Marzulli and Maibach [207]. As indicated [208], the phenomenon of sensitization is concentration dependent so sensitizing materials can be used safely below a threshold level. For example, formaldehyde can be used at 0.1% or less in most products or even up to 0.2% in a rinse-off product without producing or with minimal allergic response. Even though p-phenylenediamine showed sensitization among 8% of panelists by patch testing, in actual use in the presence of oxidizing agent and coupling agents, its concentration depletes very rapidly. Therefore, in actual hair dye use, in a short time it is below its threshold value, thus accounting for the low incidence of allergic responses among consumers of permanent hair dye products.

Quenching described by Opdyke [209] is an interesting phenomenon of sensitization. Quenching occurs when a known sensitizing agent is rendered non-sensitizing in the presence of other ingredients. Because of our current inability to predict quenching, testing of fully formulated products is preferred over testing of ingredients alone.

Phototoxicity occurs when a combination of an ingredient plus light is necessary to produce a toxic reaction. One example is photoirritation by Bergamot oil. This reaction is sometimes erroneously called photosensitization, however, it is actually a photoirritation reaction caused by 5-methoxypsoralen in the fragrance oil and light. Harber and Baer [210] determined that some tetracyclines, sulfa drugs, some coal tar components and the psoralens of fragrance oils are among the phototoxic ingredients commonly used today. Bergamot oil is derived from the rind of the orange-like fruit of citrus bergamia cultivated in the south-western part of Italy. In the 1970s it was a common component of fragrance formulations found in shampoos, lotions, creams, soaps and fine fragrances as identified by Marzulli and Maibach [211].

The mechanism of psoralen phototoxicity has been studied extensively. 5-methoxy psoralen which is only 0.33% of Bergamot oil is believed by Grange et al. [212] to be the principal phototoxic component of the oil. 5-Methoxy psoralen absorbs ultraviolet light above 310 mμ and is elevated to an excited state (free radical). The psoralen radicals link to pyrimidine bases of DNA causing the release of histamine and the subsequent reactions of inflammation (burning and blistering). In extreme cases, further complications are possible. 5-Methoxy psoralen is largely removed from Bergamot oil by distillation; nevertheless, the oil's use has declined substantially.

Other cosmetic ingredients, cited in the literature for phototoxic reactions, are 6-methyl coumarin (formerly used as a fragrance component of sun protection and facial products) and halogenated salicylanilides (previously used in antibacterial products such as deodorant soap bars) [211].

6.12.7 *Safety Considerations for Shampoo and Conditioner Products*

Shampoos and conditioners when used for their intended purpose and in the manner described on the package label are among the safest consumer products sold today. Cautionary eye warning labels appear on most medicated products and on some cosmetic brands, attesting to the fact that eye irritation can occur if some products accidentally drain or spill into the eyes. Warnings against internal consumption also appear on many shampoo labels and on a few creme rinses or hair conditioners. Nevertheless, many conditioners contain no cautionary warnings, because they are mild and of such low toxicity.

Bergfeld [213] reviewed the most frequent adverse effects of hair products from patients at the Cleveland Clinic Dermatology Department over a 10-year period, and found relatively few adverse effects from shampoos. The majority of adverse effects are due to sensitization rather than to irritation or hair breakage. Furthermore, Bergfeld attributes these few adverse effects either to preservatives or medicated ingredients of these products rather than to the active ingredients.

Ishihara [214], in 1970, surveyed five large hospitals in Japan for contact dermatitis from hair products. Only 0.2% of cases of the total number of outpatients at all dermatologic clinics were admitted for adverse reactions to any hair preparations. Only 0.008% of these adverse reactions were due to shampoos, and these few cases involved contact dermatitis. From these results, Ishihara concluded that most cases of contact dermatitis from shampoos and conditioners are not serious enough to be treated in a hospital.

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Chapter 7
Dyeing Human Hair

Abstract The different types of dyes described for human hair include, permanent or oxidation dyes, semipermanent dyes, temporary dyes or color rinses and other types of dyes either proposed for or used on human hair. The mechanism of oxidative dyeing of human hair is presented in detail describing a large number of different dye precursors and couplers and how they combine to form different dye species. Hydrogen peroxide and the new peroxymonocarbonate oxidative systems are presented. Different matrix compounds used in hair dyeing are also included. Regulatory activities related to oxidation hair dyes, described in this chapter, focus on the European community which has been the most active in the regulation of oxidation dye ingredients and provides periodic updates on the COLIPA website for safe and banned hair dye substances. Because of the increase in the aging population and the global sale of hair dye products to the graying population, a review of the initiation of hair graying including the age at which graying begins for different populations, the incidence of graying versus age in 5 year increments for different populations and graying among different geo-racial groups are also presented.

7.1 Introduction

Because of the increase in the aging population and the resultant graying of hair for all peoples of the world, the global sale of hair dye products has been increasing at a faster rate than many other hair care products. Therefore, a review of the incidence of hair graying, graying versus age and graying among different geo-racial groups is presented at the end of this chapter. Other areas of new research for this edition described in this chapter include a means to minimize hydroxyl radical in oxidative hair dyeing, a new oxidative system and photoprotection of hair proteins. Fading of artificial hair colors and effects of photofilters on fading, regulatory methods, hair shine effects and dyeing, and a novel method for producing permanent dyed hair using dye-metal ion complexes have also been included.

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There are three ways to modify the color of hair: it may be made lighter by bleaching (see Chap. 5); artificial colors may be added to the hair; or a combination of both of these methods may be employed. Adding color is the subject of this chapter. Hair coloring has been carried out for more than 2,000 years [1, 2] using various vegetable, mineral, and animal substances as coloring agents. Most of the dyes considered for human hair may be described as oxidation dyes, ionic dyes, metallic dyes, natural based hair colors, or reactive dyes.

The classification used for discussion in this chapter consists of four groups:

Permanent or oxidation dyes
Semipermanent dyes
Temporary dyes or color rinses
Other dyes

Oxidation dyes are often referred to as permanent hair dyes and are the most important of the commercial hair dyes. Permanent hair dyes generally consist of p-diamines and p-aminophenols that are oxidized by hydrogen peroxide to active intermediates [3]. These active intermediates then react inside the hair with color couplers to provide shampoo-resistant dyes.

Semipermanent products consist of nitroaromatic amines or aromatic amino nitroanthroquinone dyes [4, 5] that diffuse into and bind to the hair but do not bind firmly. Since these dyes are not firmly bound, they diffuse out of the hair with water and shampooing and can be nearly completely removed after a few (4–6) shampoos. Temporary dyes or color rinses are acid dyes [6–8] similar to those used in wool dyeing. However, because color rinses are used at room temperature, the dyes do not diffuse into the hair or bind firmly and they may be removed by a single shampooing.

Other dyes developed and described in the literature for hair include basic dyes [9], metallic dyes, reactive dyes, vegetable dyes [2], and natural-based hair colors discussed in the last part of this chapter. Wool dyeing is very different from hair dyeing because of the high temperatures involved in the former. In fact, low temperature dyeing in wool is 80–85°C. Solvent assist dyeing permits wool to be dyed at 60–70° still too high a temperature for dyeing human hair. Prototype systems have been developed based on chemistry related to that of natural melanin pigment formation [10]. These developmental systems may one day become commercial.

Most hair dyeing processes are diffusion-controlled reactions and therefore provide a “ring dyeing” effect, see Figs. 7.1 and 7.2. The ring dyeing in Fig. 7.1 was produced after 18 h reaction with methylene blue at high pH, a relatively complete dyeing process. Most commercial dyeing of hair provides a ring dyeing effect, but to a lesser extent, more like that of Fig. 7.2 produced by cetrimonium chloride for 1 h at pH 9 and stained with Rubine dye.

For forensic or commercial evaluations, light microscopy can determine whether or not hair of unknown history has been dyed with a permanent hair dye or has recently been dyed with a semipermanent dye. Human scalp hair does not generally contain pigment in the cuticle. Therefore, a light microscopic evaluation of fiber

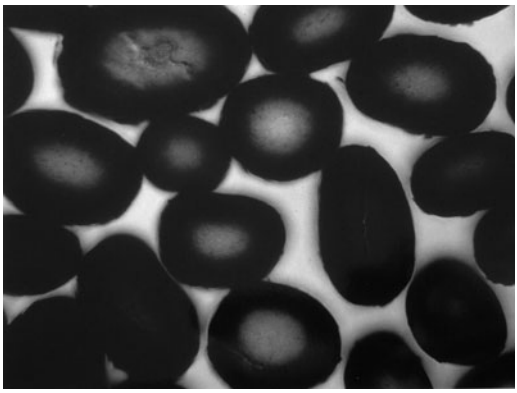


Fig. 7.1 Ring dyeing effect. Fibers treated with methylene blue (18 h at pH 9). Some of fibers show complete penetration, while others show incomplete ring dyeing. Note some of the fine fibers are less completely dyed than some of the coarser ones

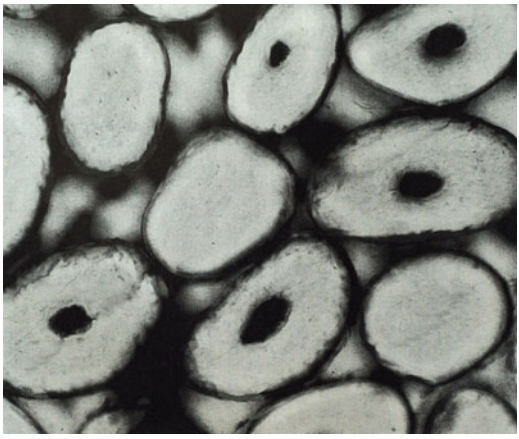


Fig. 7.2 Another illustration of "ring dyeing". Cross-sections of hair fibers treated with cetrimonium chloride (1 h pH 9) and then stained with Rubine dye after sectioning. The stain shows where the cationic surfactant has penetrated into the hair

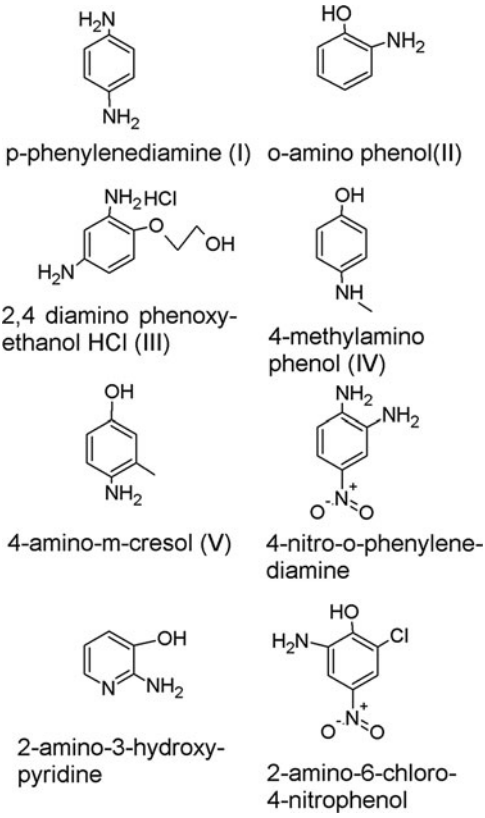
cross-sections or even an optical section can reveal whether or not the hair in question has been treated with a commercial hair dye by determining if there is dye in the cuticle. The basic physical chemistry of the interactions of ionic dyes with hair is related to that of ionic surfactants and is described in Chap. 6, including definitions for diffusion coefficients, ion affinities and experimental procedures to determine these parameters of physical chemistry.

7.2 Oxidation Dyes or Permanent Hair Dyes

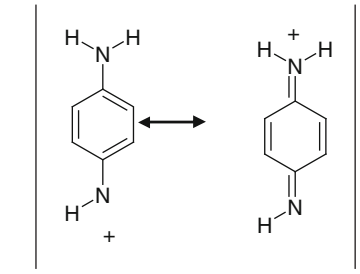
7.2.1 Compositions and Dyeing Conditions

Oxidation hair dyes consist of dye precursors that form active intermediates, dye couplers that condense with the active intermediates, an oxidizing agent (hydrogen

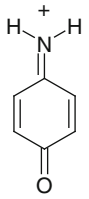
Table 7.1 Some oxidation dye precursors



peroxide), and matrix compounds consisting of surfactants, preservatives, and additives for pH adjustment and ingredients for conditioning. These reactions are usually carried out at alkaline pH, generally from 8 to 10 [2, 11–14]. By adjusting the proportions of oxidant, precursors, and couplers, the hair may be made lighter or darker in one process. Oxidation dye precursors are derivatives of aniline (see Table 7.1). Precursors are difunctional ortho- or para-diamines or aminophenols that are capable of oxidizing to diiminium (IX) or quinoniminium (X) ions, proposed by Corbett [3] as the active intermediates of this process.



Diiminium ion of p-phenylenediamine (IX)

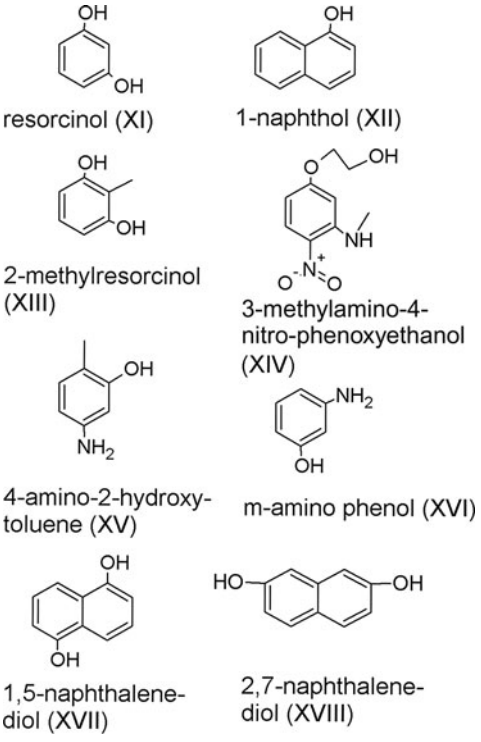


Quinoniminium ion of p-aminophenol (X)

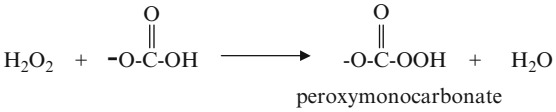
This paper [3] by Corbett is an excellent review of the chemistry of oxidative dyeing. Oxidation dye couplers are electron-rich aromatic species. They are commonly substituted resorcinols or meta-phenylenediamines, usually containing a vacant position para to the amine or phenolic group (see Table 7.2). Oxidation dye precursors, when oxidized in the absence of couplers, form colored compounds, usually gray or brown-black shades. On the other hand, couplers themselves usually produce little or no color, but in the presence of precursors and oxidizing agent, they modify the color formed by the precursor. The ingredients above are described in [2, 14–19] and on product ingredient labels.

Most oxidation dye formulations contain two or three or more ingredients that act as either dye precursors or couplers. Therefore, several reactions are involved, and multiple dye products are formed for each hair color formulation. As indicated before, hydrogen peroxide is usually the oxidizing agent of choice for oxidative hair dyeing. However, peracids [3], and autoxidation [19] or air oxidation of the highly electron-rich dye precursors or oxidation with a mixture of ammonium carbonate with hydrogen peroxide and glycine [20] have also been used. This latter system is believed to function by the formation of peroxymonocarbonate and offers some advantages [20].

Table 7.2 Some oxidation dye couplers



[a]These and other couplers are described in References 2 and or 14–19 and on product labels



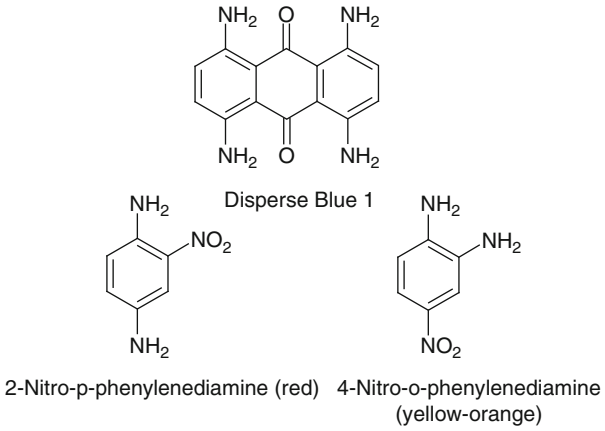
Oxidation by hydrogen peroxide in oxidation dyes is generally performed at a pH of 10 ± 0.2. This pH involves the hydroperoxide anion as the primary active oxidizing species. However, Marsh et al. [21] have shown that when redox metals such as copper or iron are present in the hair or the water supply, free radical reactions can also occur involving the very active and destructive hydroxyl radical. These same scientists also demonstrated that some of the oxidative damage by the hydroxyl free radical can be reduced by including certain chelants in the oxidative system [21]. For a more comprehensive discussion of the effects of oxidation reactions on hair see Chap. 5.

Another advantage offered by the peroxymonocarbonate system is that similar hair lightening to that of hydrogen peroxide at pH 10 can be achieved by significantly lower pH's because of peroxymonocarbonate's lower pKa (3.8 and 10.3 [22]) versus 11.75 for hydrogen peroxide [23]. The higher pH required for hydrogen peroxide is because the active species in its reactions is likely the hydroperoxide anion which is only 50% of the peroxide at its PKa, whereas the monoanionic peroxymonocarbonate species is active and it is essentially fully ionized at pH 8 and higher. Furthermore the peroxymonocarbonate system has been shown to provide maximum lightening between pH 9 and 9.5 and it decreases with further increasing pH. This effect is most likely due to the formation of the dianion (pKa 10.3) which is a less effective oxidizing agent for hair pigments.

Even though hydrogen peroxide or peroxymonocarbonate are the oxidizing agents of choice for oxidative dyeing, peracids [3], and autoxidation [19] or air oxidation of highly electron-rich dye precursors have also been used. The nature of the autoxidation process must be analogous to the self-condensation reactions described for dye precursors in the next section. Internal cyclization of the dinuclear indo dye will also occur frequently [19]. A few trisubstituted benzene derivatives and analogous naphthalenes [19, 24] and quinolines have also been described along with some of the dye products for autoxidative dyeing, but this is clearly not a preferred process.

Modern oxidation dyes sometimes contain coloring agents in addition to dye precursors and couplers; for example, direct dyes like disperse blue 1 and nitrophenylenediamines are sometimes included.

One might predict that these ingredients could enter into oxidation dye reactions, but because the strong electron-withdrawing nitro or anthraquinone groups are present, these groups should decrease the rates of oxidation and coupling of these species below that of oxidation dye reactants. Thus, these dyes probably function primarily as direct color modifiers.



Tables and data describing the colors formed by reaction of many of the precursors and couplers that are shown in Tables 7.1 and 7.2, as well as related ingredients, have been compiled by Wall [2], Tucker [8], and Corbett [3, 19].

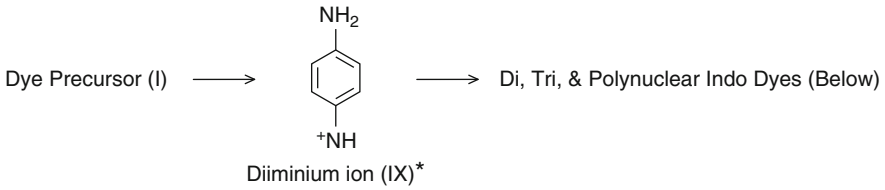
7.2.2 Summary of the Reactions of Oxidation Dyes

Table 7.3 summarizes a scheme for formation of oxidation dyes and provides some examples of the types of dyes that have been isolated from these reactions.

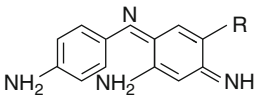
This scheme shows that a dye precursor (e.g., p-phenylenediamine) is oxidized to its corresponding diiminium ion (IX). This active intermediate then condenses with an electron-rich dye coupler, forming a dinuclear product that is oxidized to an indo dye. This reaction may stop at the dinuclear dye stage, or additional condensation-oxidation reactions may occur, forming trinuclear or even polynuclear dyes and pigments [3, 25]. More detailed mechanisms describing the formation of these and other indo dye products are presented in the next section.

Because most oxidation dye products contain 5–7 or more ingredients capable of acting as either dye couplers or precursors, mixtures of di-, tri-, and poly-nuclear indo dyes are formed in these reactions. In addition, it is conceivable that nucleophilic groups in hair might even add to the indo dyes, covalently bonding dye molecules to the hair. Penetration of the dye precursors and the couplers can occur, but penetration must be limited to the outer regions of the hair, since the condensation reactions that occur are relatively fast compared with diffusion, and the larger condensation products (at least in the hair) are resistant to shampooing.

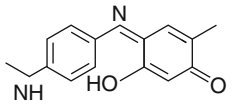
Table 7.3 Scheme and examples of indo dyes formed in oxidative hair dyeing



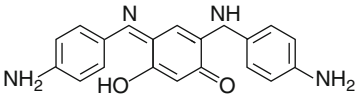
Diiminium ion (IX)*



Dinuclear indo dye from (I) and 4-Substituted m-phenylenediamines (XIX)



Polynuclear indo dye from (I) and resorcinol (XX) [25]



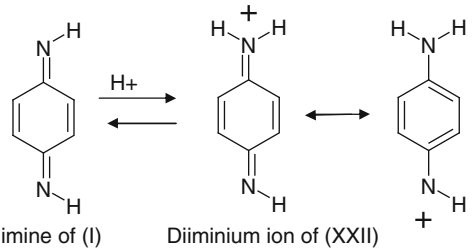
Trinuclear dye from (I) and resorcinol (XXI) [26]

[a]Of the several possible resonance forms of (IX), this one is shown in the next few sections because it enables one to visualize the mechanisms proposed to explain the products which are intended as tools for structure prediction rather than as descriptions of the molecular actions

7.2.3 Mechanisms for Oxidation Dye Reactions

7.2.3.1 The Active Intermediates in Oxidation Dye Reactions

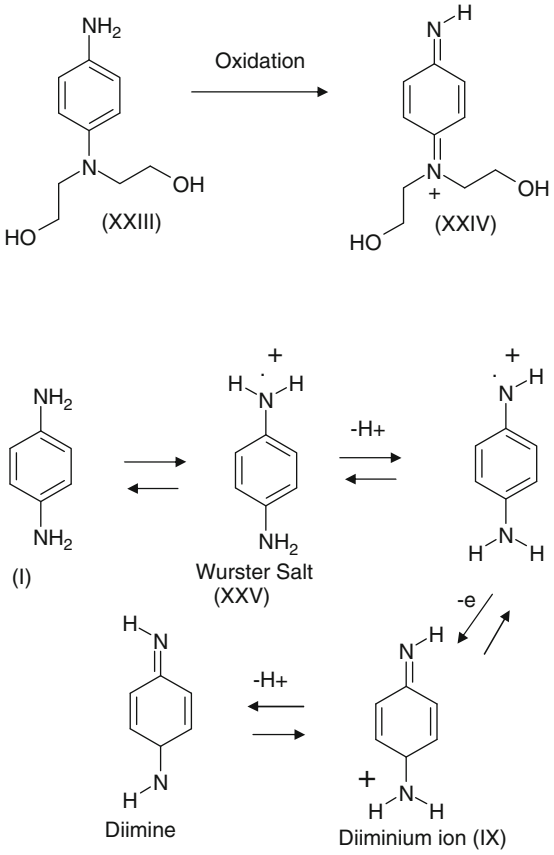
The diimine (XXII) has been described as a vital intermediate in oxidative hair dyeing [26]. Subsequently, Corbett [3] described the protonated diimine (IX) as the reactive species that actually attacks dye coupling agents, ultimately forming indo dyes.



Certainly diiminium ions are more electrophilic and are therefore more capable of serving as the active species in these reactions than diimines. As such, diiminium ions are described as the active intermediates in the mechanisms considered in the

subsequent discussions. By analogy, quinoniminium ions, such as (X), would be the active intermediates formed from ortho- and para-aminophenols. If one assumes that diimines are formed by two one-electron transfer reactions [27, 28] with the loss of two protons, and that the entire sequence occurs stepwise, then a diiminium ion is formed before diimine.

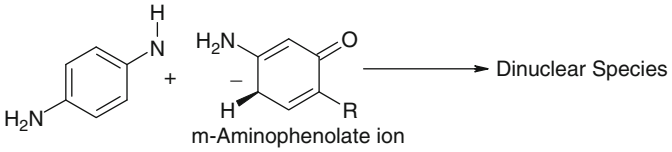
Although diimines may form in these interactions, they are not necessary intermediates for forming the di-, tri-, and polynuclear indo dyes that have been shown to form. For example, compound (XXIII), an N,N-dialkyl-substituted p-phenylenediamine, has been used in several commercial hair dyes in the past. This species should be capable of forming a diiminium ion (XXIV), although it cannot form a corresponding diimine. One might speculate that (XXIII) functions only as a dye coupler; however, related N,N-dialkyl p-phenylenediamines have been used with common dye couplers (in the absence of unsubstitued p-phenylenediamines). This finding suggests that this type of species does act as a dye precursor in oxidative hair dyeing [8, 29, 30].



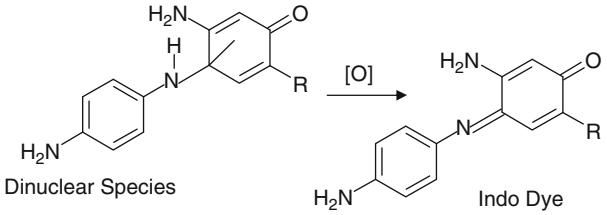
Mechanisms may also be written involving Wurster salts (XXV) to provide the di-, tri-, and polynuclear indo dyes for these reactions. Lee and Adams [31] generated the Wurster salt of p-phenylenediamine by electrochemical oxidation in buffered media. Above pH 6, the radical stability decreases rapidly, indicating the low stability of these species under hair-dyeing conditions. Therefore, the diiminium ion is more likely the active intermediate in actual hair dyeing.

For the following discussion, a five-step reaction mechanism explains the formation of di-, tri-, and polynuclear indo dyes that have been isolated from oxidation dye reactions.

Step 1: Formation of the diiminium ion from the dye precursor.
Step 2: The diiminium ion attacks a coupler (generally para to an amino or phenolic group), forming a dinuclear species.



Step 3: Oxidation of the dinuclear species to a dinuclear indo dye then occurs. If the 4 position of the indo dye is blocked (bears a substituent other than hydrogen), the reaction tends to stop at this step.
Step 4: Dye precursor or another molecule of indo dye may add by 1, 4 addition across the indo dye, forming a trinuclear or polynuclear species (see Table 7.3).



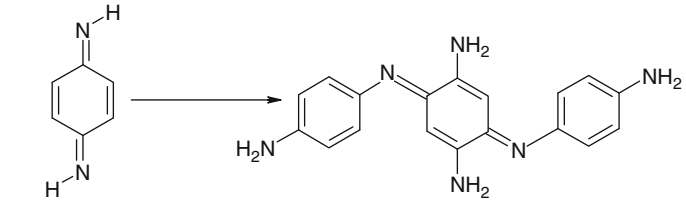
Step 5: Oxidation of trinuclear or polynuclear species to higher indo dyes occurs. Steps 4 and 5 may be repeated, forming higher polymeric dyes.

7.2.3.2 Some Products Formed in Oxidation Dye Reactions

Bandrowski's Base

Several years ago it was proposed [14, 32] that p-phenylenediamine diffuses into the fibers and is oxidized to diimine (XXII). This diimine can then condense with p-phenylenediamine to form Bandrowski's base (XXVI) a brown-black indo dye. A great deal of discussion and work concerning the actual chemical structure

[33–35] and importance of Bandrowski's base to oxidative dyeing has taken place [33, 34]. Altman and Rieger [33] and Dolinsky et al. [34] independently provided evidence that the structure shown (XXVI) represents the correct tautomer, in contrast to the structure proposed earlier by Bandrowski [35]. Altman and Rieger also suggested that Bandrowski's base is probably the end product of an undesirable side reaction in hair dyeing but is not the main colorant of hair dyed with p-phenylenediamine. Corbett [3] confirmed this conclusion by showing that modern dye couplers are several orders of magnitude more reactive to diiminium ion than is p-phenylenediamine. These facts preclude the formation of significant quantities of Bandrowski's base in modern oxidation dyes.

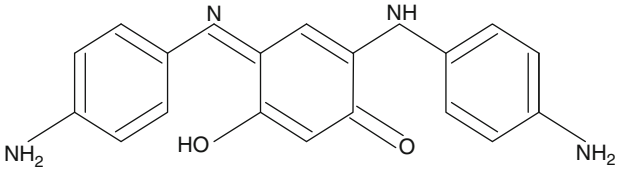


Diimine (XXII) Bandrowski's Base (XXVI)

The formation of Bandrowski's base may be described by a mechanism consistent with the general scheme described in the previous section.

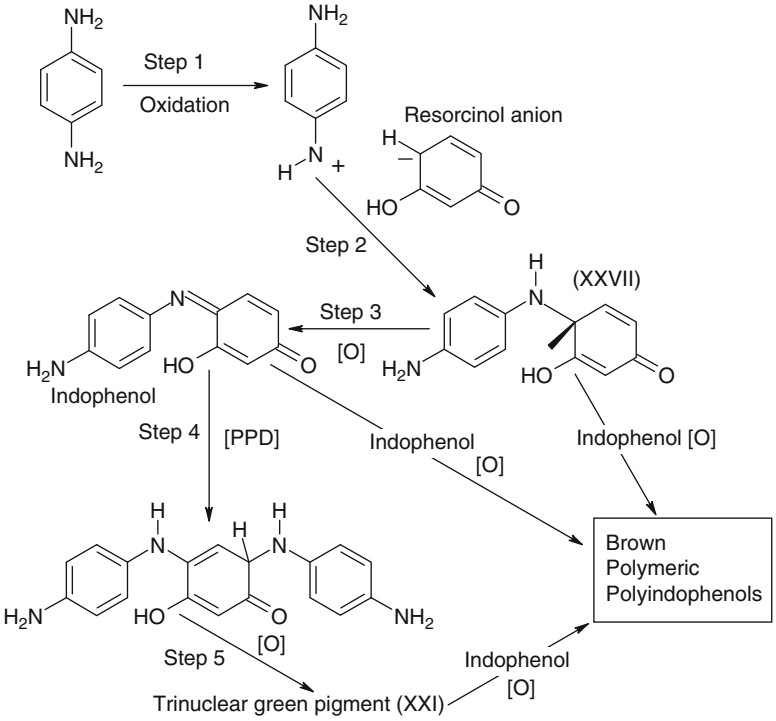
7.2.3.3 Polyindophenols from Resorcinol and P-Phenylenediamine

Resorcinol is one of the components of many oxidation dyes, and as such is probably the most commonly used oxidation dye coupler. Brody and Burns [25] have shown that p-phenylenediamine, in the absence of hair and phenols, is oxidized to Bandrowski's base. However, when resorcinol is present, polyindophenols (XX) are formed, and the formation of Bandrowski's base is effectively prevented [25]. These brown polymeric polyindophenol pigments have been identified by elemental analysis, acetyl values, and hydrolysis to p-phenylenediamine. Low-molecular-weight di- and trinuclear species were not detected by Brody and Burns. However, Shah et al. [36] isolated a green pigment from hair dyed with mixtures of p-phenylenediamine and resorcinol and identified this pigment as the trinuclear indophenol (XXI).



Trinuclear green pigment from p-phenylenediamine & resorcinol (XXI)

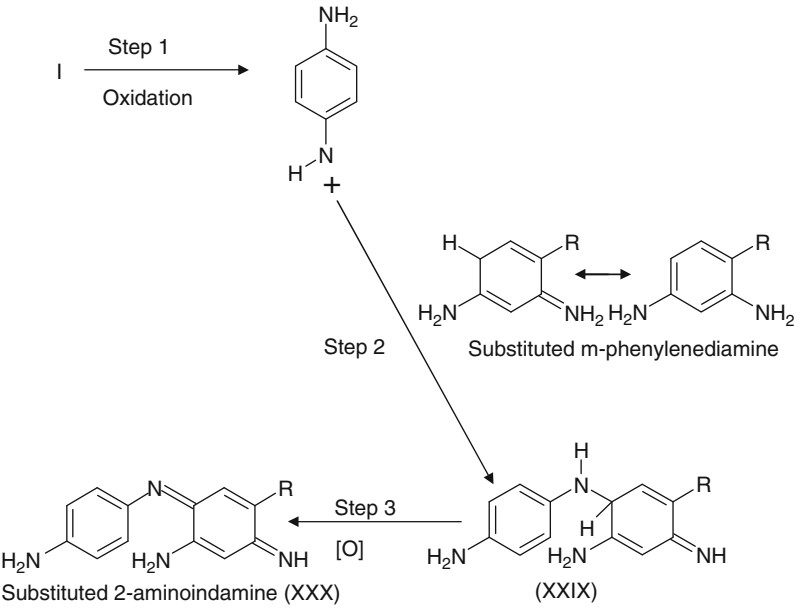
The following scheme describes the formation of the trinuclear green pigment and polyindophenols from (I) and resorcinol and is consistent with the general mechanism described earlier. This scheme suggests that the diiminium ion (IX) is the active species, and its formation has already been described. In Step 2, this electrophilic species attacks a resorcinol anion, para to the phenolic group, forming (XXVII), which is oxidized to indophenol in Step 3.



In Step 4, p-phenylenediamine adds to the indophenol in a 1,4 manner [28, 37], producing the trinuclear species (XXVIII), which is then oxidized to the trinuclear green pigment (XXI). Several routes exist for formation of polymeric indophenols. All of these routes are analogous to steps 4 and 5. Repetition of these steps results in the formation of higher polymers. Because most oxidation dyes contain both p-phenylenediamine and resorcinol, the formation of these tri- and polynuclear pigments is important to the oxidative dyeing of human hair.

7.2.3.4 Indamines from M-Phenylenediamines

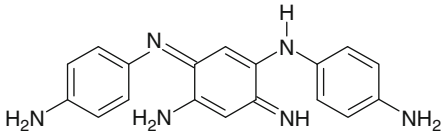
In addition to resorcinol, 4-methoxy m-phenylenediamine has been an important dye coupler, and is representative of the class of m-phenylenediamine coupling agents.



This type of dye coupler reacts with dye precursors to give blue-violet dyes that have been shown to be 2-aminoindamines [38]. Mechanistically, the formation of 2-aminoindamines is related to the formation of indophenols and fits the general scheme described earlier.

When the R group of structure (XXX) is methoxy, it represents the structural formula for the 2-aminoindamine of p-phenylenediamine and 4-methoxy m-phenylenediamine, which is a relatively stable dye. Other, less frequently used m-phenylenediamines form unstable blue dyes that cyclize internally at high humidities, forming red 2,8-diaminophenazines [3].

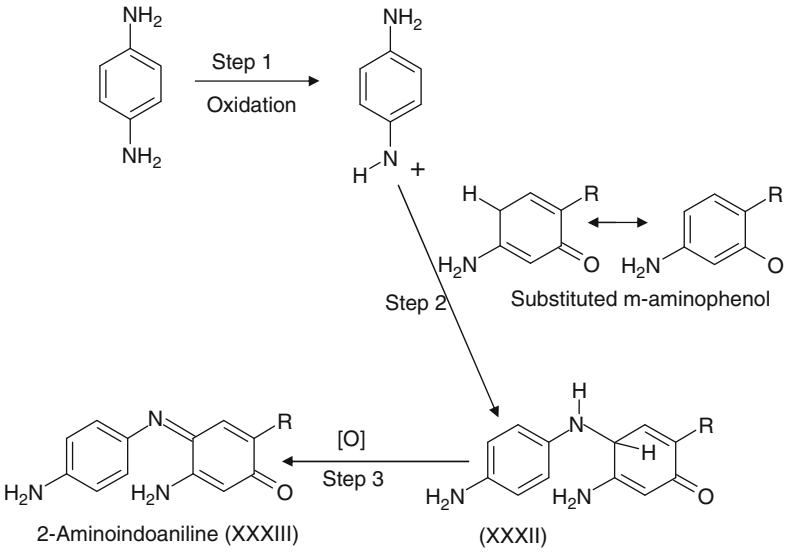
The parent compound m-phenylenediamine reacts with (I) to produce a trimer (XXXI) analogous to the trinuclear green pigment that has been isolated from resorcinol and p-phenylenediamine [3].



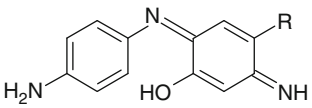
Trimer of p-phenylenediamine and m-phenylenediamine (XXXI)

7.2.3.5 Indo Dyes from M-Aminophenols

The reactions of m-aminophenols with p-phenylenediamine are similar to those described for m-diphenols and m-diamines and are summarized by the reaction scheme below.



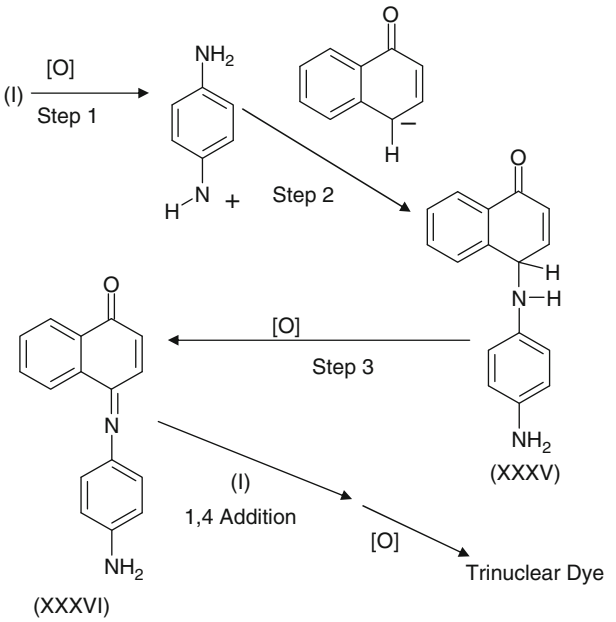
Once again (I) is oxidized to the electrophilic diiminium ion (IX) that attacks the aminophenol para to the phenolic group, forming (XXXII). This species is then oxidized to the dimeric indo dye (XXXIII) [3], analogous to indophenol. If the R substituent of (XXXII) is (almost anything but hydrogen), the reaction generally stops at the dimer stage. However, if R is hydrogen, it adds another molecule of (I) at the 4 position and is oxidized to a trimeric indo dye [3], analogous to the trimeric pigment of (I) and resorcinol; see structure (XXI). If the position para to the phenolic group is blocked, then the diiminium ion attacks para to the amino group, giving 2-hydroxyindamines [3]; see structure (XXXIV).



2-Hydroxyindamine (XXXIV)

7.2.3.6 Speculation About Dye Products Formed with Other Common Coupling Agents

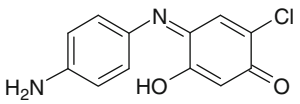
1-Naphthol is a commonly used dye coupler, and its reactions in oxidative dyeing are probably similar to those described in the previous sections; that is, the active diiminium ion attacks para to the naphthol group, forming (XXXV). Oxidation of (XXXV) should provide the indonaphthol (XXXVI).



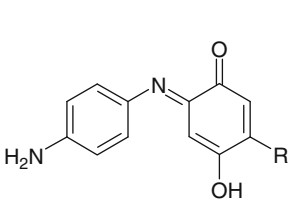
Reaction may stop at this stage, or 1, 4 addition and oxidation may occur, producing a trinuclear dye analogous to that from resorcinol and p-phenylenediamine.

Schematic reactions similar to those for resorcinol and diiminium ions can be written for pyrogallol and diiminium ions, suggesting di-, tri-, and polynuclear indophenolic dyes from the reaction of this species with dye precursors.

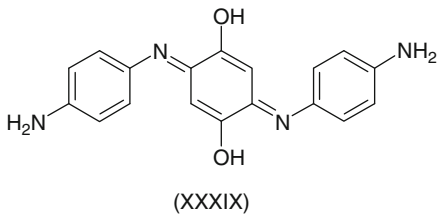
4-Chlororesorcinol, in the presence of diiminium ions, probably tends to stop at the dimeric stage, forming (XXXVII), since the positioning of the chloro group would tend to inhibit 1,4 addition.



(XXXVII)



(XXXVIII)



(XXXIX)

Hydroquinones probably form dinuclear dyes analogous to (XXXVIII) and then stop at this stage, whereas the parent compound (unsubstituted hydroquinone) probably forms analogous dinuclear species and even trinuclear dyes (XXXIX) analogous to Bandrowski's base.

7.3 Matrix Compounds

Matrix compounds in hair dyeing consist of surfactants, emulsifiers, preservatives, conditioning agents and additives for pH control/adjustment. They are essentially non-color additives that are functional in hair dyes, see Table 7.4. Vincent et al. [39] described a procedure for the extraction of matrix compounds from oxidation hair dyes to allow for the clean chromatographic separation of hair dye compounds for analysis. These same three scientists [40] have provided a reference method to allow for the identification and quantification of hair dye forming agents. This method was developed to be used for the European regulatory enforcement of these types of products.

7.4 The Formulation of Permanent Hair Dyes

Permanent hair dyes should be formulated with two different compositions or parts. The first composition is a precursor-coupler base containing surfactants (to help dissolve the precursors and couplers, to assist in spreading the dye evenly over the hair, and to help thicken the product so it does not run down the face during use), alkalinity (to facilitate the oxidation reaction), a low concentration of a reducing agent (to inhibit oxidation of the precursors by air), the precursors and couplers, and water. The second composition is an oxidizing base containing oxidizing agent, stabilizer (for the peroxide), and sometimes surfactant (for thickening during use), see Table 7.5.

To formulate the foregoing hair precursor-coupler bases, add the sulfonate and neodol to water with stirring at room temperature. Add the sodium sulfite (reducing agent-stabilizer) and then the dye precursors and couplers, stirring until they

Table 7.4 Some matrix compounds in hair dyeing

Ingredient	Function
Oleic acid	Surfactant/emulsifier
Triethanol amine	pH control
Sodium lauryl sulfate	Surfactant
Nonoxynol-12	Surfactant/emulsifier
Sodium sulfite	Antioxidant
Methyl paraben	Preservative
BHT	Antioxidant/preservative

Table 7.5 Precursor-coupler base[a]

Ingredient	Percent of ingredient for desired hair color			
	Dark brown	Light brown	Red	Black
Dodecyl benzene Sulfonate	14	14	14	14
Cocodiethanolamide	9	9	9	9
Neodol 91-2.5	6	6	6	6
Ammonium Hydroxide	6	6	6	6
Sodium sulfite	0.3	0.3	0.3	0.3
p-Phenylenediamine	0.4	–	–	0.4
o-Aminophenol	0.3	0.4	–	0.2
p-Aminophenol	–	0.4	0.4	–
4-Methyl-5-aminophenol	–	–	0.4	–
m-Aminophenol	–	–	–	0.2
Water	64	63.9	63.9	63.9

[a]The colors listed can be achieved when starting with naturally light blonde hair. The actual shade achieved depends on the starting hair color, the hair condition, and reaction time

Table 7.6 Oxidizer base

Ingredient	Percentage
Hydrogen peroxide (30%)	50
Dodecyl benzene sulfonate (50%)	33
Phosphoric acid	1
Water	16

dissolve completely. Then, add the alkalinity, followed by the amide, whereupon the product will thicken. The oxidizer base is detailed in Table 7.6. In some cases, the dye precursors and couplers should be dissolved in the amide and then the other ingredients added as above.

To formulate the oxidizer base, dissolve the sulfonate in water with stirring at room temperature. Add the phosphoric acid to the peroxide separately. Lastly, add this mixture slowly to the detergent in water with stirring.

7.5 Usage Instructions

Use of this type of product consists of three steps: the allergy test, the strand test, and application to the hair on the head.

7.5.1 The Allergy Test

Wash a small area inside the arm at the elbow. Apply a few drops of dye solution with a cotton swab to that area. Leave this area of skin uncovered for 24 h. If any itching, redness, burning, or any other allergic symptom is noticed, do not use the product. However, if there is no allergic reaction, apply the product.

7.5.2 The Strand Test

Snip a small strand of hair about ¼ in. wide (~0.6 cm), cutting it close to the scalp. Apply tape to the cut ends to hold the hairs together during treatment. Mix a small amount (1 tsp.) of precursor-coupler base and oxidizer base. Apply the dye solution to the strand of hair and wait 20 min. Then wipe the dye from the strand to check the color. If the desired shade is not dark enough, apply more dye and recheck. Continue until the desired depth of shade is achieved.

Now the consumer is ready to use the product. Mix 100 g of the precursor-coupler base with 75 g of the oxidizer base and spread it through the hair, allowing the reaction to proceed for 10–20 min or the time indicated by the strand test before rinsing thoroughly with water.

7.6 Regulatory Activities Related to Oxidation Hair Dyes

The European community has been the most active region with respect to the regulation of oxidation dye ingredients. In the late 1980s more than 150 oxidation dye couplers and precursors combined were listed for use in the European Cosmetic Directive. As of this writing, a proposal by COLIPA (Comite de Liaison Europeen de Industrie de la Parfumarie de Produits Cosmetiques et de Toilette) contains only 25 of these, see Table 7.7 and more than half of these ingredients require further testing to actually remain on this list permanently.

COLIPA has a website (www.colipa.eu/hair-dyes.html) that is worth following for anyone in the hair dye industry. On this website at the bottom of the page is a link to hair dyes that contains several important objectives and lists for those concerned with hair dyes. There is an *Assessment Strategy for Hair Dyes Safety*, and a *List of 44 positively assessed hair dye substances by the SCCP* (updated: January 2009), a *List of provisionally allowed substances* (62) (Updated: November 2006). a *List of 117 hair dye substances with an updated safety file* (Updated: November 2006), a *List of 135 banned hair dye substances* (Updated: September 2007), a *List of 49 hair dye substances proposed for ban* (Updated: September 2007), and *Guidance Document to the Commission Directive* 2007/54/EC of 29 August 2007 (ban of 85 hair dyes).

One concern however is the lack of solidarity that exists in Europe concerning regulatory matters. For example, 1-nitro-p-phenylenediamine is banned in Italy, but it is listed by COLIPA as safe, see Table 7.7. Another example of the independence of many European countries in regulatory matters is one that created confusion in the surfactant arena just a few years ago. For example, there were labeling requirements for LAS (linear alkyl benzene sulfonate) in Scandinavia, but not for the remainder of Europe. These labeling requirements created problems for marketing Pan-European products containing surfactants. Hopefully such emotional and independent decision making will not prevail in hair dyes too. The status of the

Table 7.7 Oxidation dye ingredients proposed for the future positive hair dye list by COLIPA

A. Sufficient testing done	B. Additional testing required
p-Phenylenediamine	4-Chlororesorcinol
Resorcinol	1-Naphthol
o-Aminophenol	1,5-Naphthalenediol
m-Aminophenol	2,7-Naphthalenediol
1,4-Diaminophenoxyethanol HCl	4-Methylamino phenol
2-Methylresorcinol	Hydroxybenzomorpholine
4-Amino-m-cresol	4-Amino-2-hydroxytoluene
1-Methyoxy-2-amino-4-B-hydroxyethylamino benzene	6-Amino-m-cresol
6-Amino-o-cresol	3,4-Diaminobenzoic acid
Hydroxyethyl-3,4-methylenedioxyaniline HCl	3,4-Methylenedioxyphenol
2-Aminomethyl-p-aminophenol HCl	Hydroxyethyl-p-phenylenediamine sulfate
2-Nitro-p-phenylenediamine[a]	2,4-Diamino-5-methylphenetol HCl
	2,4-Diamino-5-methylphenoxyethanol HCl

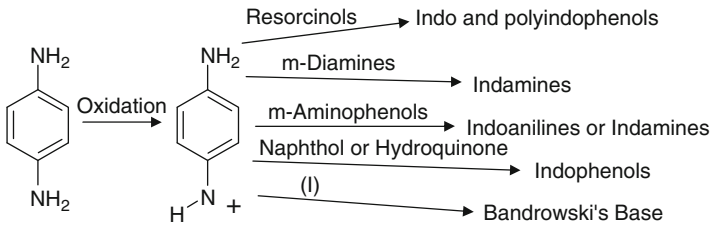
[a]Banned in Italy, but listed as safe by COLIPA

regulatory process for hair dyes in Europe is worth following especially for any company concerned with the global marketing of hair dyes.

7.7 Synopsis of Oxidation Dyeing of Human Hair

Oxidative dyeing consists of treating hair with an oxidizing system and dye precursors and couplers. Up to this time, the primary oxidizing agent is hydrogen peroxide with alkalinity (ammonia or ethanolamine) and the dye precursors and couplers. The pH of these systems is about 10 ± 0.2. The oxidizing system has two functions: One is to decolorize the hair pigments and thus lighten the hair in preparation for the colors. Second, the oxidizing system oxidizes the dye precursors to diiminium ion active ingredients as described in the previous sections. Bleaching of the hair pigments is critical to the coloring process especially for lighter or blonde shades. But, bleaching can produce damage to the hair proteins and lipids see Chap. 5.

The literature on the interactions of oxidation dyes shows that dye precursors and dye couplers are both involved. Dye precursors are oxidized to active intermediates, probably diiminium or quinoniminium species. These active intermediates react with resorcinol to form polyindophenols, trinuclear and polynuclear dyes, with m-diamines to form indamines, with m-aminophenols to form indamines; and with naphthol and hydroquinone to form indophenols. Bandrowski's base is a trinuclear species, the product of a side reaction that does not occur to a significant extent in oxidative dyeing.



Since most oxidation dyes contain three to seven components capable of acting as either dye precursors or couplers, and most contain p-phenylenediamine and resorcinol, several di-, tri-, and polynuclear colored species of this general type are formed in these reactions.

7.8 Semipermanent Hair Dyes

The term "semipermanent hair dye" refers to those products that dye the hair lasting through four to six shampoos. These products do not use hydrogen peroxide to develop the hair color [5]. For this type of product, preformed hair dyes are required. Table 7.8 depicts chemical structures of some dyes currently used in semipermanent hair dye products. To achieve the desired shade, each product contains a combination of up to as many as 18 hair dyes [41, 42] similar to those described in Table 7.8. Other ingredients in these products are matrix compounds, such as, solvents (primarily water and glycols or glycol derivatives), surfactant(s), amide, fragrance and acid or alkali for pH adjustment.

Semipermanent hair dyes are generally applied to freshly shampooed hair and allowed to remain on the hair for approximately 20 min. The hair is then rinsed with water. Often a "conditioner," is packaged with the product. After application of the dye and rinsing the conditioner is added and the hair rinsed again and dried generally without shampooing.

7.8.1 Formulation of Semipermanent Hair Dyes

To formulate the dye products described in Table 7.9, first dissolve the sulfate in water, and then add the sulfonate, the neodol and the amide while stirring. Add the dyes and stir until they are completely dissolved. Alternatively, the dyes may be dissolved in the amide and/or the neodol and then added to the anionic surfactants in water.

Table 7.8 Examples of some dyes used in semipermanent hair dye products

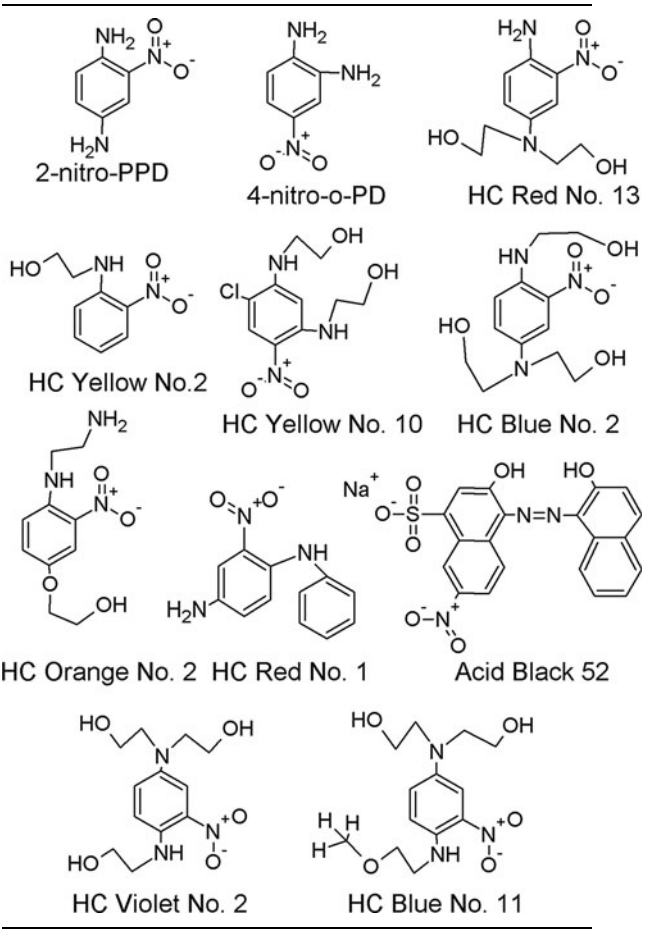


Table 7.9 Formulated semipermanent hair dyes[a]

Ingredients	Percent of ingredients for desired hair color		
	Light brown	Dark brown	Red-auburn
Cocodiethanolamide	10	10	10
NaDodecylbenzene sulfonate	4	4	4
Neodol 91-2.5	6	6	6
Sodium lauryl sulfate	2.5	2.5	2.5
2-Nitro-p-phenylenediamine	0.4	0.4	0.4
HC Red No. 3	0.2	0.2	–
HC Yellow No. 2	0.2	0.2	0.2
HC Blue No. 2	–	0.1	–
Water	76.7	76.6	76.9

[a]These colors can be achieved starting with naturally blonde hair. The actual shade will depend on the starting hair color, the condition of the hair, and the time permitted for reaction

7.8.2 Usage Instructions for Semipermanent Hair Dyes

There are three basic steps to the usage instructions for this type of product: first, the allergy test; second, the strand test (both are described under the formulation of permanent hair dyes); and third, the actual application of the product to the hair. To apply a semipermanent hair dye, first shampoo the hair, rinse, and towel dry. Thoroughly saturate the hair with the product, using plastic gloves, being careful to minimize contact of the dye solution with the scalp. Allow the product to react with the hair for about 30 min or the time indicated by the strand test. After rinsing, a crème rinse/conditioner may be added to the hair, which is then lathered and rinsed. On the other hand, the hair may be rinsed thoroughly with water, but not shampooed. It is then set and styled as usual.

In summary, semipermanent hair dyes are products that last through four to six shampoos. They are mixtures of preformed dyes generally with 10–18 dyes mixed to achieve the desired shade. These dyes are generally mononuclear, dinuclear, or trinuclear species and are usually aromatic amines, amino nitrobenzenes, or anthraquinone derivatives. These dyes generally diffuse into hair and are retained by weak polar and Van der Waals attractive forces. Therefore, the affinity of the dyestuff generally increases with increasing molecular size. Peroxide is not used to develop the color. Therefore, no "major" chemical changes occur to the fibers during this type of dyeing.

7.8.3 Color Fading and Light Fastness of Permanent and Semipermanent Dyes

7.8.3.1 Semipermanent Dyes and Rinse-Out

The hair dyes of Table 7.8 generally consist of neutral aromatic amine, nitro aromatic amine, or anthraquinone derivatives. They are all highly polar ingredients and can be classified as mono-, di-, or trinuclear (ring) dyes. Wong [43] studied the kinetics of dye removal from hair for this type of hair dye. He concluded that under all conditions the larger, trinuclear dyes rinse more slowly from hair than the smaller, mononuclear dyes.

For both bleached and unbleached hair, Wong [43] showed that dye rinse-out for small dye molecules (corresponding to the mononuclear species) of semipermanent hair dyes is diffusion controlled with relatively weak dye-to-hair interactions. Han et al. [44] confirmed this finding in a study of the diffusion of HC Red 3 (Table 7.8) into and out of hair. For a discussion of techniques to determine diffusion coefficients, see Chap. 6. These workers found essentially no hysteresis in the adsorption vs. desorption kinetics, suggesting weak binding between this mononuclear dye and hair. Han et al. [44] indicated that HC Red 3 has a pK_a of 3.7. Therefore, this dye is not positively charged under hair-dyeing

conditions, but is neutral. Thus charge-charge interactions are not involved in the binding of this dye to hair. This factor helps to explain the weak binding found between this dye and hair.

Wong [43] also found that the larger trinuclear dyes, analogous to those of Table 7.8, have a higher affinity for hair than the simple mononuclear dyes undoubtedly arising from a larger number of polar and Van der Waals binding sites between dye and hair.

The principles of this study by Wong are being utilized today in semipermanent hair dye products in the following manner. It is well known that diffusion into hair and removal of dye are faster in weathered tip ends than in the root ends [5]. Thus, blends of dyes are used not only to obtain the right blend at root and tip, but to provide a more even wash fastness in both root and tip ends. For example, blends of single ring dyes diffuse more readily into and are retained more readily in root ends, whereas blends of dinuclear and trinuclear dyes are retained more readily in tip ends [45]. Thus the proper blending of mononuclear and dinuclear with trinuclear dyes will provide a more even wash fastness to both root and tip regions of hair.

Han et al. [44] further found that the diffusion coefficient of the mononuclear HC Red 3 increased with pH, with dye concentration (1.0–5.0 g/l), and with increasing temperature (25–60°C). When the dye bath solvent was changed from water to 50 volume percent aqueous ethanol dye uptake decreased. However, the diffusion coefficients remained similar in magnitude. The pH effect can be explained by increased swelling of the hair. The dye concentration and temperature effects are consistent with expectation for a diffusion-controlled interaction. The solvent effect occurs because the dye is more soluble in the ethanol-water system than in water alone, thereby increasing the affinity of dye for the solvent phase relative to the keratin, causing more of the dye to partition into the aqueous-ethanol phase and less into the hair.

Blankenburg and Philippen [46], using a scanning photometer microscope, studied the reaction of this same dye with hair. These scientists demonstrated maximum absorption of dye near the fiber exterior. Whereas at longer dyeing times the dyestuff concentration in the center of the fiber increased. In all cases, ring dyeing was observed; see Figs. 7.1 and 7.2. These results are consistent with a diffusion-controlled process.

Wong [43] found that for the smaller mononuclear dyes, bleaching increased the rate of dye rinse-out. However, for the larger dyes, the rinse-out rate decreased with a small amount of bleaching, and went through a minimum until the rinse-out rate began to increase with bleaching. Wong suggested that with a small amount of bleaching the larger dyes are able to reach more hindered positions in the hair substrate. Therefore, with a small amount of bleaching the dyes bind more firmly and are more difficult to remove with rinsing. However, with additional bleaching, the hair becomes more penetrable, and the rinse-out rate of the larger dyes increases but never approaches the rinse-out rates for smaller dyes.

7.8.3.2 Dye Color and Light Stability of Semipermanent Dyes

Corbett [45] related dye color and light stability of some semipermanent hair dyes to dye structure. With regard to light-fastness, Corbett demonstrated that for monosubstituted nitrobenzene dyes, the ortho-substituted dyes are the most stable to light and the para-substituted the least light-stable. For nitrobenzene dyes containing two electron-donating substituents, those with 2,5 substitution are the most light stable, while those with 2,4 and 3,4 substitution are less stable to light.

7.8.3.3 The Mechanism of Fading of Highly Colored Indo Dyes

Although this phenomenon has not been studied at length, Corbett [3] proposed that fading of indo dyes most likely involves the addition of aromatic moities to dinuclear indo dyes, together with hydrolytic degradation to p-diamines and hydroxybenzoquinones that further degrade.

7.8.3.4 Fading of Permanent Hair Dyes by Shampoos and Light

Red or auburn hair dyes have been shown to fade more than other shades. Pyrazole derivatives such as 1-hydroxyethyl-4,5-diamino pyrazole sulfate produce the most vivid red colors although non-pyrazole red dyes are generally based on 4-amino-2-hydroxy toluene or 2-methyl-1-napthol as red couplers [47]. Furthermore, color fading has been shown to be greatest by UVB and least by IR. For example, the color fading order is: UVB $>$ UVA $>$ Visible $>$ IR [44]. However, these relative fading effects in actual practice have been found to be very different from this ranking because of the differences in the relative intensities of the various portions of natural sunlight in different parts of the world. As a result, the contributions of UVB and UVA depends on radiation time (63% at 16 h and 27% at 48 h), and the greatest effect is from visible light [48]. Therefore blocking UV light can produce a significant decrease in color fading but will not completely suppress color loss.

Locke and Jachowicz [49] demonstrated that greater fading or color loss is produced by a combination of shampooing and light radiation versus light radiation alone. Furthermore, these scientists concluded that color fading is related to the type of hair used. For example, the greatest fading occurs with natural white or bleached hair compared with brown hair. Furthermore, they calculated that use of a UVB photofilter such as octyl methoxy cinnamate on hair at a level as high as 30 mg/gm hair will absorb less than 25% of the total UV radiation, but UVA absorbers will absorb about 40% of UV at the same high concentration.

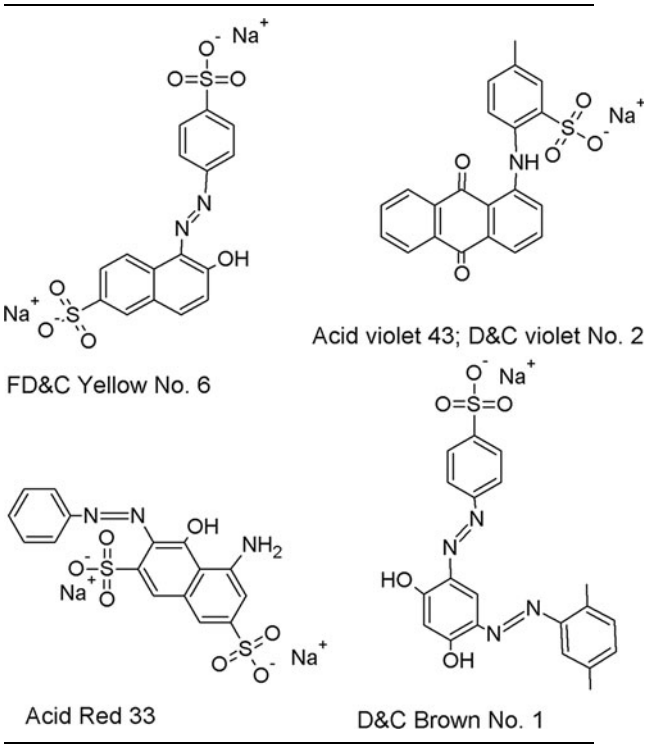
7.8.4 *Analysis of Semipermanent Hair Dyes*

Several scientific studies have been concerned with the application of high-performance liquid chromatography for analysis of direct dyes in semipermanent hair coloring products primarily for quality control purposes [42, 50]. This technique has been used successfully for the complete separation of 18 dyes in a standard mixture. It has also been applied to the separation and analysis of these dyes in eight commercial hair coloring products.

7.9 Temporary Hair Dyes or Color Rinses

The objective of temporary hair dyes is to provide color to the hair; color that is capable of being shampooed out of the hair with a single shampooing. Table 7.10 depicts structures for a few hair-coloring ingredients used in today's hair rinses. A large number of hair color ingredients previously used in color rinses are described in the article by Wall on hair dyes [51]. Each color rinse product consists

Table 7.10 Some hair color ingredients used in color rinse products



of a mixture of color additives, either among those described in Table 7.10 or similar FD&C or D&C colors. Generally two to five color ingredients are mixed to achieve the desired shade [51], because a single ingredient generally will not provide the desired color to the hair. Two dyes are sometimes used to provide tints for gray hair; four to five dyes are generally mixed to achieve reds, browns, or black.

These products are usually applied to freshly shampooed hair and combed through. An alternative is to spray the product onto the hair and comb it into the hair to achieve even distribution of the dyes. The hair is then set and dried without rinsing to minimize penetration of dyes into the fibers. The dyes used in color rinses are generally larger molecular species than those used in semipermanent hair dye products. Color rinse dyes are generally anionic or acid dyes, see Table 7.10, and are similar to those used in wool dyeing. These dye ingredients are selected to provide maximum water solubility and minimum penetration so they can be shampooed out of the hair. Wool dyeing is very different from hair dyeing primarily because of the temperatures employed. In fact, low temperature dyeing in wool is 80–85°C. Solvent assist dyeing permits dyeing wool at 60–70°C, which is still too high for human hair. For a more complete discussion of the dyeing of wool fiber, see the book *Wool Dyeing* edited by D.M. Lewis [52].

Some other dyes used in this type of product are direct black 51, direct red 80, acid black 2, D&C yellow No. 10, and other FD&C and D&C dyes.

7.9.1 Formulation of Color Rinses

Temporary hair dye products frequently contain thickeners, a surfactant, sometimes a hair-setting polymer, and a buffer or acid such as tartaric, acetic, or citric to provide an acidic medium for application of the dyes to the hair. To make the hair rinses described in Table 7.11, first hydrate the hydroxyethylcellulose (0.7 g) with 49 g of water by stirring. Next, add the neodol and the nonoxynol. Then add the remaining water followed by the buffer. Next, slowly dissolve the dyes in the product with stirring. Finally, add the cetrimonium chloride and stir until it is completely dissolved.

7.9.2 Usage of Color Rinses

First shampoo the hair with a good cleaning shampoo. Rinse the hair thoroughly and towel dry. Thoroughly saturate the hair with the product, using plastic gloves if desired, being careful to minimize contact with the scalp. Dry the hair and style as desired.

Table 7.11 Prototype hair rinse formulations[a]

Ingredients	Percent of ingredients for desired hair color		
	Brown	Red	White
Nonoxynol-9	1.0	1.0	1.0
Hydroxyethylcellulose(HHR)	0.7	0.7	0.7
Cetrimonium chloride	0.6	0.6	0.6
Neodol 91-2.5	0.5	0.5	0.5
Citric acid trihydrate	0.5	–	0.5
Trisodium phosphate	–	0.3	–
Direct black 51	0.5	0.01	–
Acid violet 43	0.04	0.03	–
Direct red 80	0.03	0.05	–
Acid orange 24	0.04	0.02	–
External D&C violet 2	–	–	0.03
D&C red 33	–	–	0.01
FD&C yellow 6	–	–	0.005
D&C yellow 10	–	–	0.005
Water	96.54	96.79	96.65

7.10 Other Dyes for Hair

7.10.1 Metallic Dyes

Salts of several metals including lead, silver, bismuth, cobalt, copper, iron, and mercury have been used in the past for dyeing hair [53]. Among these metallic dyes, lead dyes are the only ones in commercial use today. Lead dyes contain lead acetate and sulfur and react with hair to darken it slowly, presumably forming lead-sulfur complexes in the cuticle layers. The listing of lead acetate as a hair color additive in cosmetics in described in this Federal Register listing [54]. These products are popular among men because of the slow gradual buildup of color (Table 7.12). However, shades are limited for lead dyes, and the dye can react if treated subsequently with bleaches, permanent waves, and even with certain other hair dyes [16] (Table 7.12).

7.10.2 Formulation of a Lead Acetate-Sulfur Hair Dye

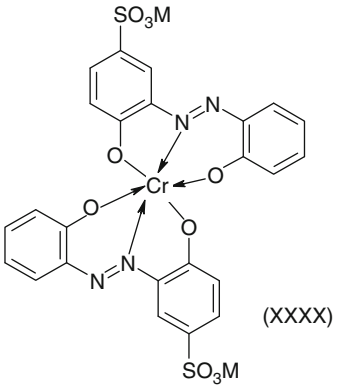
Dissolve the lead acetate in water with stirring. Disperse the sulfur in propylene glycol and add this dispersion to the lead acetate in water while stirring vigorously. Continue to stir while adding the fragrance and preservative that is previously dissolved in alcohol and the surfactant.

Another form of metallic dye is called premetalized dyes. These compounds are metal complexes of anionic dyes with chromium, cobalt, or some other metal,

Table 7.12 Lead acetate-sulfur hair dye

Ingredient	Percentage
Sulfur (finely divided)	1.0
Lead acetate	1.0
Nonoxynol-9	0.8
Denatonium benzoate	0.5
Fragrance	0.2
Propylene glycol	20.0
Ethanol	3.0
Water	73.5

generally in a ratio of 1:2 (metal:dye); see structure (XXXX) [55–57]. Some trade names are Irgalan, Cibalan, Lanasyn, Carbolan, and Isolan. Premetalized dyes have been patented and described for use with hair [58, 59]. Premetalized dyes are often classified as acid dyes rather than as metallic dyes, even though from substantivity and bonding considerations they are probably more like metallic dyes. The use of premetalized dye in the presence of an alcohol (benzyl or amyl) is called solvent assist dyeing [56]. Solvent assist dyeing is an interesting technique that produces a larger uptake of dye relative to a pure aqueous solvent and has been described in patents on human hair.



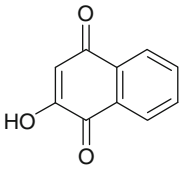
(XXXX)

7.10.3 Novel Permanent Dye Using a Dye-Metal Ion Complex

Ochiai et al. [60] reported that permanent dyes can be developed in hair using dye-metal ion complexes. These scientists used aluminum chloride as the metal ion which was allowed to penetrate into the hair so that the aluminum ion could complex with the acid dyes in the hair. Benzyl alcohol and ethanol were employed as penetration enhancers to provide for deeper penetration of the dyes. The advantage to this type of system, if it is effective, is that it would appear to provide color permanence to the hair without oxidative damage.

7.10.4 Vegetable Dyes

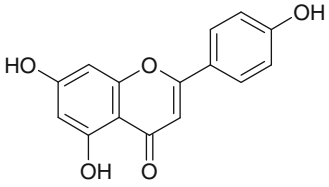
Natural organic substances from plants are the earliest known hair dyes. But, of the many substances of this type that have been tried over the years, only henna and camomile are currently used to a significant commercial extent [2]. The active coloring material of henna (Lawsone) is 2-hydroxy-1, 4 naphthaquinone. The structure of this active dye ingredient was established by Tommasi [59] and Cox [61].



2-Hydroxy-1, 4-naphthaquinone (henna)

This substance is the principal dyeing agent of the shrub henna, known as Egyptian privet. Henna has been used for dyeing hair and staining nails since ancient times in Egypt [1]. This dye is found in the leaves of the plant and is usually extracted with aqueous sodium bicarbonate. Henna produces yellow to reddish shades in proteins and is normally applied in acidic media. The nonionized (acid) form of henna is yellow while the ionized form is reddish-orange. Although the more deeply colored form of henna is available at higher concentrations at alkaline pH, henna dyes hair better at acidic pH. Amro et al. [62] proposed that protonated groups on the hair fiber complex with lawsone anions. Therefore, acidic pH is optimal to create a higher concentration of protonated sites on the hair to attach to the ionized lawsone in solution. When the ionized form of lawsone is removed from solution, additional lawsone ionizes to maintain equilibrium and thus to dye hair the reddish shade characteristic of henna dyed hair.

The active coloring substance from camomile flowers is a polyhydroxy flavone, 4′,5,7-trihydroxy flavone [2]. This substance is also found in parsley; and its common name is apiginin [63].



4',5,7-Trihydroxy flavone (camomile)

Other polyhydroxy flavones exist in plants [59]. These flavones are usually combined as glucosides or rhamnosides and are generally yellow. These materials have been used for dyeing cloth and hair. For dyeing cloth, these dyes are usually

mordanted with chromium, tin, or iron salts. This mordanting process changes the color as well as the binding character of the dye.

These two dyestuffs, henna and camomile, are chemically related by the alpha-, beta-unsaturated grouping. This group is capable of undergoing 1,4 addition reactions with free amino or other nucleophilic groups of the side chain residues of hair proteins. The review by Wall [2] describes vegetable dyes in greater detail, including their history, sources, active ingredients, and even dyeing conditions.

7.10.5 Natural-Based Oxidative Hair Coloring

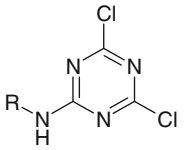
Natural hair dyeing processes have been described in the literature based on 3,4 dihydroxyphenylalanine (dopa) [10]. Natural pheomelanin type dyes begin with the oxidation of DOPA to dopaquinone which then reacts with cysteine, a nucleophile to ultimately form the natural red hair pigments. Brown et al. [10] found that by beginning with the oxidation of DOPA and incorporating sulfur-containing nucleophiles in the process, a wide range of shades can be produced on hair that are acceptable for hair dyeing. Oxidants such as atmospheric oxygen work, although the combination of hydrogen peroxide and iodide ions appears to be more effective [64–66].

An intense black eumelanin type pigment is produced by reacting DOPA with controlled amounts of potassium ferricyanide. 8-Hydroxy-1,4-dihydrobenzothiazine or thio substituted catechols which are simple analogs of intermediates of the melanic pathways when oxidized with different at specific pH conditions provide different colors similar to those of permanent hair dyes [10]. Sometimes when these catechol or benzothiazine intermediates are oxidized in the presence of oxidation dye nucleophiles they provide permanent hair dye colors. These systems are still developmental and have not been commercialized, but do appear to offer promise for the future.

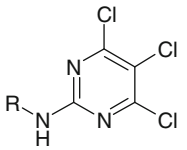
7.10.6 Fiber Reactive Dyes

A fiber-reactive dye binds to the hair or wool through covalent bonds. These reactions generally involve either nucleophilic displacement by amino, guanidino, hydroxyl, or sulfhydryl groups of the keratin on a dyestuff containing either a labile halogen or sulfate grouping. In addition, nucleophilic addition onto a dyestuff containing an activated olefinic linkage can also be used for permanent binding. Fiber reactive dyes have not been used commercially for dyeing human hair. Nevertheless, these dyes offer a novel approach to permanent dyeing. A few examples of this type of dye are described in Table 7.13. Fiber-reactive dyes will react with unreduced keratin. However, prior reduction provides additional

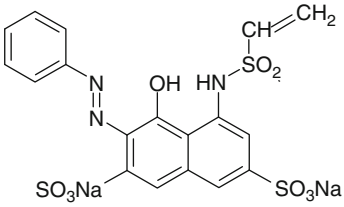
Table 7.13 Some examples of fiber-reactive dyes used in wool dyeing



Dichlorotriazine type



Trichloroprimidine type



An Activated Olefin Type

mercaptan groups for reaction with the dye and therefore enhances dyeing. For additional information, see the articles by Brown [13], Stead [55], and by Shansky [67] and the references therein.

7.11 Photoprotection of Hair by Hair Dyes

Pande et al. [68] demonstrated that hair dyes (both oxidation and semi-permanent) grant a photoprotective effect to hair proteins providing a significant decrease in cortical damage as shown by tensile testing. This reduction in damage is greater the darker the dyes used. The fact that this effect can be seen in the tensile properties proves that this photo-protection effect of hair dyes extends down into the cortical proteins.

7.12 Hair Dyeing and Luster

Hair shine is basically a ratio of specular to diffuse light scattering. Dark hair usually appears shinier than lighter hair. This is because part of the light is reflected at the fiber surface, and part enters the fiber. The light entering the fiber is scattered by reflecting off irregularities of the interior. When the light reemerges from the fiber interior, the diffuse component is increased decreasing hair shine. If the fiber is colored or dyed, some of this diffuse component is absorbed before reemerging,

reducing it. In this manner hair that has been dyed makes the fibers shinier [69]. See the section on hair luster or shine in Chap. 10 for additional details on hair shine.

Keis et al. [69] studied the effect of natural hair pigmentation on hair luster (shine) using a goniophotometer. This study confirmed that increasing hair color reduces light scattering and increases luster. These same scientists also examined dyed hair and found a similar but more complicated picture. Dye composition, concentration and penetration depth must be taken into consideration to account for the results. In addition, the luster of hair of different colors is perceived differently by the human eye adding further complications. However, Lefaudeux et al. [70] described a method for hair luster based on polarization imaging that they suggest is consistent for different hair colors.

7.13 Safety Considerations for Hair Dyes

Corbett has reviewed the general toxicology of hair dyes [5, 71]. Mutagenicity-carcinogenicity of hair dyes has been reviewed by Kirkland [72]. Bergfeld [73], Ishihara [74], and Bourgeois-Spinasse [75] reported clinical observations of adverse reactions with hair dyes. See also the section entitled, *Regulation of oxidation hair dye intermediates* earlier in this chapter. This discussion consists of a synopsis of these toxicological reviews and reports.

As described earlier in the section on regulation of oxidation dyes, the European community has been the most active region in the world with respect to the safety and regulation of oxidation dye ingredients. COLIPA (Comite de Liaison Europeen de Industrie de la Parfumarie de Produits Cosmetiques et de Toilette) is a very active group in Europe that is dealing with the regulation and safety testing requirements for permanent hair dye ingredients. Anyone concerned with manufacturing and marketing hair dyes should be aware and keep aware of the writings and conclusions of this group (see the discussion on COLIPA earlier in this chapter for details).

The primary toxicological concerns of hair dyes, primarily oxidation hair dyes, are with contact dermatitis and long-term "potential" systemic effects [5]. Of all hair products, the most sensitizing are the paradiamine oxidation dyes [75]. Furthermore, the most sensitizing ingredients of these products are p-phenylenediamine, p-toluenediamine sulfate, and o-chloro-p-phenylenediamine, although other related aromatic amines have been shown to provide some sensitizing potential [74].

Since p-phenylenediamine is the major component of oxidation hair dyes and oxidation dyes are the most widely used of all hair dyes, p-phenylenediamine is the sensitizer of prime concern. Corbett [5] pointed out that while p-phenylenediamine is a strong allergin, the incidence of allergic reactions by oxidation dyes is of low frequency and the reaction when observed is generally mild. Corbett suggests that this low incidence of sensitization is due to the rapid reaction and decreasing concentration of this reactive ingredient during actual hair dyeing [5].

The sensitization symptoms from oxidation dyes are a discrete dermatitis at the periphery of the scalp and on the edges of the ears. Itching scalp, and occasional eruptions occur on the face, especially around the eyelids [74]. Eruptions on the trunk and limbs are rare [74].

Usually symptoms appear several hours after the dyeing process has begun. Treatment of this allergic reaction consists of oxidation of residual paradiamine with peroxide in saline solution. This treatment should be followed by application of corticoid creams or lotions [75]. Allergic reaction to hair color rinses is rare [67]; however, a few incidents of allergic reaction to semipermanent hair dyes have been reported [71].

Misra et al. [76] provided data to suggest that the skin toxicity of p-phenylenediamine might relate to its interaction with lipophilic biomolecules and the subsequent biotransformation products. Gagliardi et al. [77] examined the alleged claim that exposure to vapors of p-phenylenediamine in hair dressing salons might cause lung allergies. Their results and conclusions suggest that this is not the case. They conclude that it is unreasonable to consider that hairdressers are at risk to p-phenylenediamine-induced asthma.

Long-term toxicological risk from semipermanent hair dyes is low [5, 71]. However, 2-nitro-p-phenylenediamine and 4-nitro-o-phenylenediamine currently used in Europe in semipermanent hair dyes, but not in the U.S; have been tested extensively for potential carcinogenicity. This latter dye was shown to be non-carcinogenic in animal feeding studies. But, the former diamine caused adenomas in rats, but only at the highest feeding level. At moderate and low feeding levels, this dye did not produce adenomas [71].

Several hair dye ingredients, primarily permanent hair dye components, have been tested for potential carcinogenicity [5, 72]. The impetus for this testing arose from the finding several years ago that some aromatic diamines provide a positive reaction as mutagens [5, 71] in the Ames bacterial screening assay against the bacterium Salmonella typhimurium [76].

Corbett summarized the details of the mutagenicity screening of oxidation dye components. He concluded that the Ames test for aromatic diamines does not correlate as well with results of carcinogenicity in animal feeding studies, as for other chemical types [5]. Both Corbett [5] and Kirkland [72] summarized the results of several common hair dye ingredients in in-vitro mutation tests, in dominant lethal animal testing, and in epidemiological studies. One of these testing programs consisted of a CTFA study involving more than 35 oxidation dye components and 34 textile dyes used in temporary hair color products. From this work and other studies, the FDA determined (in October l979) that all hair dye products containing 2,4-diamino anisole must bear a cancer-warning label [77–79]. Industry responded by removing this ingredient from oxidation hair dyes.

Corbett concluded that “all animal studies completed to date have shown hair dyes to be safe for their intended use.” Kirkland [72] concluded that “epidemiological and human monitoring studies have not detected any such risk (carcinogenicity) in exposed human populations.” However, Kirkland suggested that more controlled epidemiological studies and more extensive monitoring of exposed populations are in order.

7.14 Gray Hair and Graying of Human Hair

Gray hair is described in this Chapter on hair dyeing because the gray hair audience is one of the largest groups that dye their hair. It is unfortunate that so little is known about the physical and chemical properties and distinctions between gray hair and highly pigmented hair fibers. For a discussion on the current status of this subject see the section entitled, *Hair Pigment Structure and Chemical Oxidation*, in Chap. 5.

Nevertheless, data on the incidence of graying versus age and some of the background and speculation on possible causes of graying in this Chapter should be useful to those involved in research and development of hair dyes. This section begins with a discussion on the formation of gray hair followed by the incidence of gray hair by sex, age, and geo-racial group. Next, the relationship between gray hair and other important hair parameters such as diameter and hair density is presented. Finally, the reactivity of gray hair and the phenomenon of sudden graying are described.

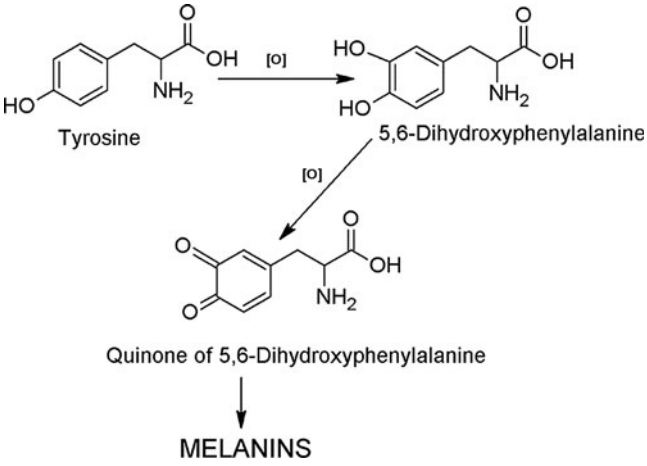
7.14.1 The Process of Graying of Scalp Hair

Gray hair relates to the size and distribution of the melanin granules as well as the types of pigments in the fibers; see Chap. 5 for additional details on hair pigments. The medulla does seem to play some role in gray hair, as suggested by Nagase et al. [80] by scattering light through a change in refractive index at the air to hair interface of medullary "pores". This effect is analogous to the phenomenon that occurs in the genetic abnormality of pili annulati also known as ringed hair that provides the appearance of bands or rings of silver or gray and dark regions along the fiber axis, see Chap. 1 for additional details.

Gray hair is dependent on the production of less pigment in the individual hairs with advancing age. It is usually associated with middle age; however, graying can begin in one's early 20's as described later in this chapter. Graying generally begins in the temple region and then spreads to the vertex or crown and finally to the remainder of the scalp usually affecting the occipital region (back of the skull) last. The formation of hair pigments takes place in the melanocytes (pigment producing cells) in the bulb of the follicle starting with the amino acid tyrosine as described in Chap. 5. The melanin type pigments are incorporated into the hair fiber as large granules in the zone of keratinization, see Chap. 1.

Biochemical control of the graying process is still not completely understood; however, Kukita [81] suggested that gray hair is produced by a gradual decrease in the function of melanin producing cells. Tobin and Paus [82] suggested that melanocytes in the region of the hair bulb function through 7–15 different hair cycles to produce pigmented hairs for up to four decades or longer. Each group of melanocytes in each follicle functions independently of melanocytes in neighboring

hairs. Graying results from a decrease and the eventual termination of the activity of the enzyme tyrosinase in the lower bulb [81, 82]. This enzyme is involved in the reaction scheme called Raper's scheme for the formation of 5, 6-dihydroxyphenylalanine and then its quinone from the amino acid tyrosine. These species then react further to produce the melanin pigments.



Kukita [81] demonstrated that the onset of tyrosinase activity coincides with the appearance of melanocytes during anagen. Its activity increases rapidly with increasing numbers of melanocytes. Tobin et al. [83] summarized the regulation of coat color in hairy mammals by POMC-derived peptides (α-melanocyte stimulating hormone, adrenocorticotropic hormone and β-Endorphin). The expression of these peptides and the melanocyte-1 receptor (MC-1R) are confined to specific regions of the hair follicle and are adjusted or controlled in their effectiveness during the hair growth cycle. β-Endorphin has also been shown by Tobin et al. [83]to play a role in the regulation of human hair pigmentation.

Commo et al. [84] studying hair follicles of pigmented hair, gray hair and white hair determined that the loss of hair shaft melanin is associated with a decrease in both hair bulb melanin content and hair bulb melanocytes population density. Arck et al. [85] suggested a free radical theory of graying involving high oxidative stress and apoptosis in the graying process. This hypothesis suggests that radiation, inflammation and psycho-emotional stresses are involved in graying. Therefore, increases in any of these stresses will speed up the graying process. On the other hand, any reduction in these stresses should lead to delaying the graying process. This hypothesis seems to fit the suggestion by Tobin and Paus [82] that the initiation of graying begins about 5 years later for Asians and even later for Africans compared with Caucasians, because darker pigmentation in skin and hair surrounding the hair bulb should provide some protection against sunlight radiation effects or stress.

Tobin and Paus [82] suggested that the active melanocytes in the hair bulb are replaced with "seedlings" seven to fifteen times in a human lifetime. Therefore, a

small number of melanocytes in the hair bulb function for up to 10 years at an exceptionally high melanogenic activity. This intense oxidative activity generates large amounts of reactive oxygen species (ROS). If these ROS are not actively removed over time, then DNA (nuclear and mitochondrial) damage results producing mutations that induce de-pigmentation or graying.

7.14.2 The Onset and Incidence of Graying

Tobin and Paus [82] predicted that the average age of the onset of gray hair for Caucasians is in the mid-30s, while for Asians it is in the late 30s and for those of African descent it occurs in the mid-40s. These scientists are talking about the age of the onset of complete graying rather than the age of onset of a few gray hairs which occurs earlier than these specified ages.

Keogh and Walsh [86] conducted a large study on the incidence of graying in 1965 in Australia. This study included subjects from ages 25 to 60 plus. These scientists found no significant difference in the graying of hair of males versus females, so they combined the male and female data and separated the data into 5 year age increments. This study contained a total of 8,720 persons including 6,653 men and 2,067 women. This paper did not specify racial characteristics of the group. However, the data is from Victoria, Australia, therefore it likely consists largely or totally of Caucasians.

Keogh and Walsh included persons who had dyed their hair and those who had not dyed it. When the hair had been dyed or suspected of being dyed they relied on the subject's own statement regarding the true color and degree of grayness prior to dyeing because preliminary trials showed the observers to be in substantial agreement with ratings by trained observers.

7.14.3 The Effect of Hair Color on the Perception of Graying

The data of Table 7.14 summarizes the data of Keogh and Walsh [86] comparing % any gray and % complete gray versus the "true color of the hair" categorized as Fair, Medium and Dark. Significant differences were observed in the ability to see graying of these three hair color types.

For the data of Table 7.14, the numbers of subjects are all relatively large especially in the three lowest age groups. Each of these groups contains more than 300 subjects. The data of age groups 42.5 through 52.5 are all 205 subjects or larger and for age group 57.2, the number of subjects is 137 or greater. But, in age group 62.5 the number of subjects in each hair color group is only 26 or fewer. Therefore, the data of this oldest age group are the least reliable.

These authors [86] analyzed the data by logistic regression and concluded that at approximately age 49 (48.6%) about 50% of this population has 50% gray hair. This

Table 7.14 Age and graying of Caucasian scalp hair; calculated by means polynomial modeling from data by Keogh and Walsh [86]

% Any detectable gray				% Total or completely gray			
Age	Fair	Medium	Dark	Age	Fair	Medium	Dark
27.5	3.4	9.4	27.7	27.5	0.4	0	0.0
32.5	19.4	34.0	47.4	32.5	0.6	0	0.5
37.5	39.2	54.1	63.9	37.5	0.9	2.2	0.54
42.5	60.1	70.0	77.3	42.5	4.6	3.3	2.6
47.5	79.1	82.1	87.2	47.5	8.9	7.0	7.4
52.5	93.6	90.7	94.1	52.5	23.9	17.4	13.8
57.5	100	96.1	97.7	57.5	42.3	30.1	18.6
62.5	97.8	98.6	98.2	62.5	50.0	23.3	16.8

The following model equations were used to calculate the above values from the Keogh and Walsh data for % any gray. All models contain $R^2 = 0.99$ or greater and $p < 0.0001$

% Any gray (fair) $= -102.446 + 3.832\text{Age} - 0.0632(\text{Age-45})^2 - 0.0037(\text{Age-45})^3$

% Any gray (medium) $= -36.80 + 2.518\text{Age} - 0.07342(\text{Age-45})^2$

% Any gray (dark) $= -8.013 + 2.013\text{Age} - 0.0641(\text{Age-45})^2$

For % completely gray higher order polynomial models were used, but were not effective for extrapolating to zero gray. An effective model could not be constructed for fair hair; therefore, the Keogh and Walsh data were used. For both medium and dark hair $R^2 = 0.99$ and $p < 0.02$

% completely gray (medium) $= -26.69 + 0.6917\text{Age} + 0.1116(\text{Age-45})^2 + 0.00699(\text{Age-45})^3 - 0.0002867(\text{Age-45})^4 - 2.316\text{e-}5(\text{Age-45})^5$

% completely gray (dark) $= -39.165 + 0.9749\text{Age} + 0.0511(\text{Age-45})^2 - 0.001606(\text{Age-45})^3 - 0.0001277(\text{Age-45})^4$

statement has been widely quoted and mis-quoted to apply to all populations. It would appear that the age of 49 for 50% gray hair should apply to Caucasian populations. If the conclusion of Tobin and Paus [82] is correct about graying in other geo-racial groups, one would expect it to be about 5 years later for Asians and 10 years later for those of African descent.

Chi Square analysis shows significant differences between fair and medium to dark haired groups. In contrast to little graying, this perception of complete graying appears earlier in the fair haired group than in the other two hair color groups especially after age 40. This effect likely arises because a few dark hairs will stand out more readily against a light background of gray hair than a few light hairs against a light gray background.

7.14.4 The Age that Graying Begins

To test at what ages the detection of graying begins, the Keogh and Walsh [86] data for the three classes of hair color were examined because these data started at age 25. Plots were made of the mid-point age of each age group versus the % any gray, providing the % any gray data of Table 7.14. The graphical data were clearly not linear, but displayed a distinct curvature. JMP statistical software from SAS was used to provide the best fitting polynomial models for all three hair color types (fair,

medium and dark). Graphs were constructed from the prediction data of the best equations with the smoothest-least interrupted curves in the lower age groups and predictions made to as low an age as feasible.

From this analysis, the detection of any gray hair for the dark haired persons begins at about age 21–22, for the medium color hair persons it begins at about age 25 and for the fair haired persons the detection of graying begins at about age 26. deBerker et al. [87] have described where graying occurs at earlier ages than suggested by these data. This, "premature graying" has been defined as the "onset of graying before 20 years of age" [87] in Caucasians, before 30 years of age in people of African descent [82, 87] and before 25 years of age in Asians [82, 87]. This definition agrees well with the conclusions from the statistical equations to predict the beginning of graying in Caucasians. The conditions of premature graying are generally related to diseases [87] such as pernicious anaemia, hyperthyroidism and certain autoimmune diseases or even premature cardiovascular disease as shown by Eisenstein and Edelstein [88].

7.14.5 A Second Large Study of Graying of Hair

Another large data pool of graying versus age is from the Copenhagen city heart study by Schnohr et al. [89]. The authors of this study do not specify racial characteristics of the subjects. Because of the location I assume that the subjects are largely or totally Caucasians. One advantage to the Copenhagen study is that it contained such large numbers (5,837 men and 7,163 women (13,000 total subjects)). The disadvantages of this study are that the age groups were in 10 year increments and it did not include any subjects younger than 30 years of age. In addition, the authors separated out those subjects who dyed their hair and did not determine grayness on those subjects. The Copenhagen study separated all subjects into those with no gray hair, those with little gray hair, moderate gray hair and total gray/white hair and also those with dyed hair and those with wigs.

To determine if the data from these two large studies could be combined, I assumed that the percentage of gray haired subjects in the dyed hair group was the same as in the non-dyed group and added the two together. With this assumption and combining the data of men and women, the data of % any gray and % total or complete gray corresponded well with the data of Keogh and Walsh [86], that is the differences were generally within plus or minus 2%.

7.14.6 Best Estimates of % Little Gray, % Moderate Gray and % Completely or Total Gray in 5 Year Age Increments

Data from all three hair color types of the Keogh and Walsh [86] study were combined with the data of men and women in the Copenhagen study. The Keogh

and Walsh study went down to age 25 while the Copenhagen study [87] only to age 35 (30–39). The Keogh and Walsh study used few subjects at age 55 and above; whereas the Copenhagen study used many more subjects in the higher age groups. So, where possible, the Keogh and Walsh data were used for ages 20–30 and the Copenhagen study was used for ages 60–70. Means of the combined studies were used for ages 35–55. The data of Table 7.15 summarizes the analyses of these combined studies on the incidence of graying with additional explanations as part of that table.

No comparable data on graying of hair versus age based on large numbers of Asians or Africans could be found in the literature. Therefore, assuming that these conclusions of Tobin and Paus [82] are correct: that graying begins with Asians and Africans about 5 years and 10 years later than with Caucasians and that once graying begins the rate of graying is the same for these three geo-racial groups, then one can approximate the incidence of graying versus age for Asians and Africans by examining the data of n–14 and 7–15 and moving each data point back 5 years for Asians and 10 years (to older ages) for Africans. Until sufficient data can be obtained for large numbers of Asians and those of African descent these approximations should be useful.

Table 7.15 Percent little gray, percent moderate gray and percent total gray of the scalp hair of Caucasians at different ages; calculated by polynomial modeling from data by Keogh and Walsh [86] and Schnohr et al. [89]

Age	% little gray	% moderate gray	% total gray (Eqn)	% any gray (Eqn)
20	0	0	0	0
25	6.3	0[a]	0	6.3
30	22.5	0.6[a]	0	23.1
35	43.5	3.7	0.5	42.8
40	52.3	9.3	2.7	61.4
45	54.7	16.4	6.0	76.2
50	52.2	22.7	10.3	86.0
55	46.2	30.1	15.7	90.9
60	38.0	33.7	22.2	92.4
65	29.1	36.8	29.8	93.3
70	20.8	37.5	38.5	98.0

% little gray is from a cubic equation for the Copenhagen study data of ages 35–70 and for ages 20–30 by subtraction. For the cubic model $R^2 = 0.99$, $p = 0.0015$ and the root mean square error = 2.157: % little gray = $47.74 + 0.1569\text{Age} - 0.1046(\text{Age-}43.98)^2 + 0.001867(\text{Age-}43.98)^3$

% moderate gray was obtained by subtraction of % total gray + % little gray from % any gray

% total gray is from a quadratic equation of data combined from the Keogh and Walsh and Copenhagen studies where $R^2 = 0.994$, $p < 0.0001$ and root mean square error is 1.167. The equation is: % total gray = $-28.35 + 0.7625\text{Age} + 0.0215(\text{Age-}45)^2$

% any gray is from a quartic model from data of Keogh and Walsh and the Copenhagen studies combined where $R^2 = 0.996$ and $p < 0.0001$ and the root mean square error is 2.8799. Equation: % any gray = $-35.58 + 2.484\text{Age} - 0.103(\text{Age-}45)^2 - 0.0007748(\text{Age-}45)^3 + 9.267*10^{-5}(\text{Age-}45)^4$

[a]This data point was from linear regression analysis and extrapolation from ages 35 to 70

7.14.7 Hair Graying and Hair Fiber Diameter

There is conflicting evidence in the literature as to whether gray hairs are coarser or finer than highly pigmented hairs. Nevertheless, current evidence appears to favor that gray-white hairs are coarser than highly pigmented hairs, but the evidence is not overwhelming. This subject is covered in detail in Chap. 5 in the section entitled, *Hair Pigment Structure and Chemical Oxidation*. For leading references into this area see the papers by Hollfelder et al. [90], Gao and Bedell [91] and Van Neste [92] which are summarized in that section in Chap. 5.

7.14.8 Hair Graying and Scalp Hair Density Versus Age

This is area with a major GAP and requires investigation. My conclusion is that not considering diseases like alopecia areata (described later), hair density in gray areas should differ very little from those in areas with highly pigmented hairs on the same scalp. Consider that Graying begins in the temple region in the early 20s (as mentioned above) and yet the temple region is one of the last scalp regions to be affected by male pattern alopecia (MPA). Graying does not appear to be affected by female pattern alopecia (FPA). Therefore, MPA and FPA appear independent of graying therefore I would conclude that there is little difference in scalp hair density of gray and pigmented hair. I offer the caution that this is a conclusion, not a fact, and needs to be either confirmed or denied by additional research.

7.14.9 Sensitivity of Gray Hair to Light Radiation and Free Radical Reactions

Less pigmented hairs, e.g., gray hairs, blonde hair or bleached hairs are also more sensitive to light radiation than heavily pigmented hairs [48, 91]. Therefore, lightly pigmented gray hairs when exposed to ultraviolet radiation for a sufficient period will show lower levels of cystine and correspondingly higher levels of cysteic acid particularly in their outer layers as compared to heavily pigmented hairs. In addition ultraviolet or free radical damage to tryptophan, as shown by McMillen and Jachowicz [93], and other amino acids occurs at a faster rate in lightly pigmented gray hairs versus heavily pigmented hair. Pande et al. [68] showed that dyed hair when exposed to ultraviolet light provides higher tensile properties than non-dyed hair. This experiment demonstrates that hair pigments provide photochemical protection to hair. Therefore gray hairs will show greater damage to sunlight and ultraviolet light compared with more highly pigmented hairs (see Chaps. 5, 9 and 10 for additional information).

7.14.10 Sudden Graying–Whitening of Hair

Jelinek [94] reviewed several historical and literary reports of sudden graying of hair. The one that this author has heard most frequently is that of Sir Thomas More, whose hair was reported to have turned white the night before his execution. A note in the British Medical Journal [95] on the subject of "sudden whitening of hair" relates this condition to alopecia areata. Sabouraud [96] reported that white hairs are often retained in patches of alopecia areata. This report [96] attributes sudden whitening to a disease process related to alopecia areatea. Sudden graying-whitening involves the entire scalp, wherein the dark hairs are shed over a short time period, but most of the white or gray hairs are retained providing the appearance of sudden graying.

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Chapter 8
Polymers in Hair Products

Abstract Polymers have become increasingly important components of cosmetics over the past few decades. The original uses of polymers in hair care were as fixative agents and viscosity controlling additives; however, new polymers today are also used for hair conditioning and for the development of new style control products. Polymer substantivity to hair fibers increases with molecular size, with an increasing number of polar group attachments and especially with an increasing number of cationic groups for attachment to the negatively charged surface of hair fibers. From an anionic shampoo medium the cationic charge on polymers is neutralized and the adsorbing species is essentially a neutral or negatively charged species. The most successful silicone conditioning polymers for hair care have been used in both shampoo and conditioner compositions. Dimethicones in shampoos condition undamaged or lightly damaged hair better than they condition highly damaged, bleached hair or even tip ends because neutral hydrophobic conditioning agents adsorb more readily to an undamaged hydrophobic surface than to a damaged highly polar hair surface. New block co-polymers and a fairly large number of new cationic polymers have been introduced into hair care recently, while fractal polymers (highly irregular shapes) and nanoparticles have been developed and are receiving attention for potential use in hair care.

8.1 Introduction

Several new, useful fixative polymers have been introduced into the cosmetic industry over the past decade to provide improved hair spray formulations in response to the 55% VOC regulation for hair sprays and hair shines that were originally imposed by the California Air Resources Board. In addition, new cationic co-polymers have become available that employ three and sometimes four co-monomers. Long chain alkyl groups have been introduced into several of these

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and into some other cationic polymers to provide hydrophobicity. Further trends in hair care polymers are summarized in a paper by Lockhead [1].

Over the past two decades, the use of silicone polymers in two in one shampoos has become increasingly important commercially. Several different types of silicone polymers have been introduced into the cosmetic industry in the past decade and our knowledge on the adsorption, conditioning and stabilization of silicones from anionic shampoo systems has increased greatly. As a result, a section summarizing the literature on silicone polymers including their interactions with hair and with other ingredients especially in shampoo systems is included in this chapter.

New block co-polymers and a fairly large number of new cationic polymers have been introduced into hair care this past decade. Fractal polymers or dendrimers (with irregular shapes and surfaces) are receiving attention for potential use in hair care formulations and the area of nanogels and the generation and use of nanoparticles in hair cosmetics is also an area that is beginning to receive attention and is described in this chapter. These areas (fractal polymers and nanoparticles) should prove to be fruitful in the future. However, at this time these innovations are in their infancy for our industry. The above subjects provide the basis for most of the new material in this section on polymers and polymer chemistry in hair products.

Polymers have become increasingly important components of cosmetics over the past few decades. Their more important uses are as primary ingredients or adjuncts in shampoos, conditioning products, styling products (lotions and gels), mousses, and hair sprays. They have been used to condition hair [2, 3] and to improve the substantivity of other ingredients to hair [4, 5], to improve combing [2], manageability [2, 3], body [6], and curl retention [1, 3, 7]; to thicken formulations [8, 9]; and to improve emulsion stability [8].

Because of environmental concerns, a great deal of research has taken place to develop polymers that release water more readily. As suggested earlier, the goal is to provide polymers that are more compatible with water with the aim of developing spray products that can be formulated with lower levels of volatile organic compounds (VOC) and as a consequence more water. The driving force at this time has become the standards proposed by the California Air Resources Board (CARB) that has proposed that the maximum allowable VOC emissions for hairsprays be:

- 80% by January 1, 1993 and
- 55% first proposed for January 1, 1998 and later extended to June 1, 1999.

Since a few other states have adopted the 55% VOC standard for hair sprays and shines, creative formulation and science is necessary to market these products. VOC's in hairsprays in the U.S. have become an issue while hydrocarbon propellants with ethanol solvent are commonly used in some other parts of the world. Thus, the section on hair sprays has been expanded to summarize issues and concerns created by this regulation and to describe how these are being addressed.

Other CARB regulations relevant to hair care are:

Hair mousses, 6% VOC – by December 31, 2002 and Hair styling gels, 6% VOC – by January 1, 1994. These regulations specify a 1-year period after the effective dates above for any company to sell existing products that do not comply with these regulations in the San Francisco Bay Area Air Quality Management District. Hairsprays are an exception. Hairsprays that are not in compliance must be off the shelves by the effective dates.

The following subjects are of special relevance to the application of polymers in hair products and thus are the focus of this chapter:

- The binding interactions of polymers to hair;
- The chemical nature of polymers used in hair products;
- In situ polymerization reaction mechanisms;
- Rheological or flow properties of polymer solutions; and
- Film formation and adhesional properties of polymers.

The major emphasis in this chapter is on the first three of these subjects – the chemical and/or binding interactions of polymers to hair; the chemical nature of hair sprays, setting products, and mousses; and in situ polymerization reactions in hair. Although the rheological properties of polymer solutions are especially important to formula viscosity, and to the sensory perceptions of cosmetics, they will not be emphasized here. It suffices to say that cellulosic ethers [8, 9] are probably the most important thickening agents in hair products, and ethoxylated esters and carboxy vinyl polymers are also important.

For hair sprays, polymer setting products, and polymeric conditioners, film properties as well as the ability of the polymer solution to spread over the fiber surface is important to product performance. The ability of the polymer to spread over the hair surface is governed by its solution viscosity and the wettability of the fiber surface in contact with the polymer solution. For optimum spreading, low solution viscosity is important, and both polar and dispersion interactions have been shown to be important to the ease of spreading over hair fiber surfaces [10]. The surface of cosmetically unaltered hair is generally considered to be hydrophobic, whereas the cortex is more hydrophilic. Kamath et al. [10] have shown that both bleaching and reduction of hair increase the wettability of hair, making its surface more hydrophilic. For a more thorough treatment of wettability and the spreading of liquids on solids, see the following references [10–13].

8.2 The Binding of Preformed Polymers to Hair

Chapter 6 describes the work of Steinhardt and Harris and the affinities of organic acids [14] and quaternary ammonium hydroxide compounds [15] to keratin fibers. It illustrates the importance of increasing molecular size and even non-primary bonds to the substantivity of ingredients to hair. In the case of polymeric ingredients, these same principles are operative, and even more important. Chapter 6 also describes the important interactions leading to deposition of conditioning

ingredients from both anionic and cationic surfactant solutions, including an hypothesis that considers a continuum between a charge driven adsorption process and a hydrophobically driven process. This same hypothesis is not repeated in the current discussion; however, it is highly relevant to the discussion which focuses on factors that are important to the deposition of polymeric ingredients onto human hair.

8.2.1 Chemical Bonding and Substantivity

It is convenient to consider three extreme types of bonds between polymer and hair.

- Primary valence bonds (ionic and covalent bonds).
- Polar interactions (primarily hydrogen bonds).
- Dispersion forces (Van der Waals attractive forces).

It should be noted that bond classifications of this type are not rigorous, and the transition from one type to another is sometimes gradual. Therefore, intermediate bond types do exist [16], although for simplicity in the following discussion a rigorous classification of bond type is presented.

Primary valence bonds include ionic and covalent bonds and are the strongest binding forces. Both of these types of bonds generally provide bond energies of about 50–200 kcal/mol [17]. Ionic bonds are extremely important to the interactions of polymeric cationic ingredients and hair, whereas covalent bonds are probably involved between polymer and hair in certain in-situ polymerization reactions described later in this chapter.

Hydrogen bonds are the most important polar interactions and are the next strongest binding forces, with bond energies generally of the order of 4–10 kcal/mol [17]. These bonds are about an order of magnitude less than covalent or ionic bonds and are important to the binding of polymers containing polyalcohol or polyamide units to hair. Polypeptides and proteins are two examples where hydrogen bonding is important.

Dispersion forces or Van der Waals attractions provide bond energies generally of the order of 1 kcal/mol [18] about two orders of magnitude less than covalent or ionic bonds. Van der Waals attractive forces are relatively weak and are dipolar in nature. Since electrons are in constant motion, at any instant in time, the electron distribution is probably distorted, creating a small dipole. This momentary dipole can affect the electron distribution in an adjacent molecule. If contact is just right, attraction is induced [19]. These attractive forces are short-range and act only between the surfaces of molecules. Therefore, the total strength of Van der Waals bonding increases with molecular surface area, as an approximation with increasing molecular size. Therefore, in polymers van der Waals bonding can approach the strength of primary valence bonds.

For an interaction between molecules, entropy is inversely related to the amount of structural organization of the total system. More randomness or less structural organization of the system is always preferred. In many cases, less structural organization is

required to bind a large hydrophobic molecule to a hair surface than to emulsify it into a lipid-aqueous system. Thus, entropy can provide a driving force to push large hydrophobic polymers out of the solvent system and onto the hair fiber surface.

8.2.2 *Molecular Size and Substantivity*

Mark [20, 21] described the forces involved in multiple polar and dispersion binding in polymers by means of molar cohesions (see Table 8.1). These data show that in polymers of relatively low molecular weight, 10,000 Da, the cohesive

Table 8.1 Polar and dispersion forces in polymers

Polymer	Structural unit	Approximate molar cohesions for units shown (kcal/mol)
Polyethylene	$(-CH_2-CH_2-)$	1.0
Polyisopropylene	$(-CH_2CH(CH_3)-CH_2CH(CH_3)-)$	1.2
Polystyrene	$(-CH_2CH(C_6H_5)-CH_2CH(C_6H_5)-)$	4.0
Polyvinyl alcohol	$(-CH_2CH(OH)-CH_2CH(OH)-)$	4.8
Polyamides	$(-CH_2CH(C{=}O)NH_2-CH_2CH(C{=}O)NH_2-)$	5.8

[a]Molar cohesions listed are actually for a chain length of 5 Å. The structural units shown above are approximately 4.6 Å long, assuming a constant carbon-carbon bond length of 1.54 Å [22]

energy approaches that of primary chemical bonds. Therefore, by analogy with the affinity of surfactants and dyes to hair (Chap. 6), one may predict the importance of molecular size to the substantivity of polymers to hair.

Obviously, multiple sites for attachment of even stronger bonds such as polar and especially primary valence bonds are even more important to substantivity. Multiple covalent attachment sites could conceivably occur via in situ polymerization reactions and with bi-functional cross-linking agents (see Chap. 4). However for pragmatic reasons, this is not nearly as important as multiple ionic attachments to hair as can occur with cationic polymers.

The appropriate spacing of groups in the polymer so that maximum bonding can occur, especially to ionic and polar groups on the keratin structure, is also important to substantively. As a first approximation, the maximum frequency of primary bonds and the maximum molecular size will provide maximum substantivity.

8.2.3 Isoelectric Point of Hair and Polymer Substantivity

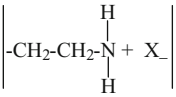
Although polymers may penetrate to a limited extent into human hair [23], the key interactions between hair and most polymers occur at or near the fiber surface. Obviously, lower molecular weight polymers are more prone to penetrate than high molecular weight polymers and damaged hair is more penetrable than chemically unaltered hair.

Since ionic bonds are the most important primary valence bonds for binding to hair, under low temperature conditions in an aqueous or aqueous alcohol system, the net charge at the fiber surface is critical to polymer hair interactions. Wilkerson has shown that unaltered human hair has an isoelectric point near pH 3.67 [24]. Therefore the surface of hair bears a net negative charge at all pH values above its isoelectric point. Since most cosmetic hair treatments are formulated above this pH, cationics ingredients are attracted to hair more readily than anionics, and polycationics are more substantive to hair than polyanionics.

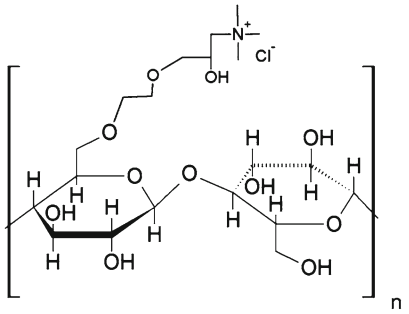
8.2.4 Desorption and Breaking Multiple Bonds

Faucher et al. [25] demonstrated that desorption of a polymeric cationic cellulose (polymer JR) (see Table 8.2) from hair is slower than would be expected from a simple diffusional release predicted by the square root of time law [26]. These scientists suggested that desorption of a polymer occurs only after all sites of attachment are broken. Statistically, the process of breaking all attachments simultaneously is of low probability. Therefore, one would expect high substantivity and a slow rate of release with increasing molecular size and increasing primary valence bonding sites.

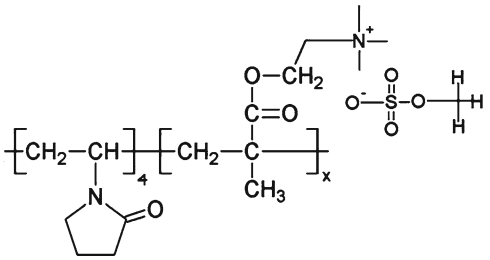
Table 8.2 Approximate structures for three cationic polymers used in hair care products



Polyethyleneimine (PEI) with a charge density of 176, assuming 25% protonated at pH =8 [42].



Quaternized hydroxyethyl cellulose with a charge density of 689 (polyquaternium-10).



Quaternized copolymer of PVP and dimethyl aminoethyl methacrylate with a charge density of 616 (Polyquaternium-11).

8.3 Penetration of Polymers into Hair

Low-molecular-weight polypeptides [27] (M_n = 1,000) and polyethyleneimine (M_n = 600) [28] have been shown to diffuse into hair. Somewhat larger polypeptides (M_n = 10,000) [27] and polymer JR, with an average molecular weight of 250,000 [23], have also been reported to penetrate into hair. The polymer JR study involved bleached hair. These data suggest that penetration is limited to about 10% of the hair after 7 days and about an order of magnitude less in unaltered hair [25]. Sorption of a higher-molecular-weight JR polymer (average molecular weight of 600,000) by bleached hair is similar to the smaller polymer by unaltered hair.

It appears that some limited penetration into human hair can occur by the lower-molecular-weight species of low molecular weight polymers (less than 10,000 Da).

Larger polymers, up to 500,000 Da, may even contain species (smaller) that can diffuse into the cuticle and perhaps further. Intercellular diffusion or diffusion through the non-keratin regions is probably the preferred route for these large molecules (see Chap. 6). If the hair is degraded sufficiently or if the degree of polymerization for the polymer provides a broad distribution, intracellular diffusion may also occur. However, it is highly unlikely that large polymers penetrate to a significant extent into human hair. Neutral or anionic polymers have not been studied for penetration effects. However, as a first approximation, one might draw similar conclusions with regard to the size and extent of penetration of these polymers also.

8.4 Cationic Polymers and Their Interactions with Hair

Because of their high degree of substantivity, cationic polymers are one of the more important types of polymers used in hair products. They are even useful in shampoos in addition to their use in hair conditioners. Their major asset, high substantivity, is also a potential problem, because they can be so substantive that they are sometimes difficult to remove from hair by shampooing.

Cationic ingredients in general are highly substantive to hair because of hair's low isoelectric point (IP). The IP of cosmetically unaltered hair is approximately pH 3.67 [24] and even lower in bleached hair. Thus, at any pH above the isoelectric, the surface of hair bears a net negative charge; therefore positively charged (cationic) ingredients are attracted to it.

Even monofunctional cationics are substantive to hair to the extent that they resist removal by water rinsing. For example, stearyl benzyl dimethyl ammonium chloride and distearyl dimonium chloride are major active ingredients in creme rinse products because they are substantive to water rinsing and condition the hair fiber surface.

Dye staining tests [29, 30] shows that substantivity of monofunctional cationics to water rinsing does not occur unless the hydrocarbon portion is approximately 8–10 carbon atoms or longer. This effect occurs because sufficient Van der Waals attractive forces in addition to the electrostatic bond must exist to bind the molecule to the fiber in the presence of the aqueous phase. As the molecular size of the cationic structure is increased, even greater sorption and substantivity result [30]. This enhanced substantivity is partly due to an increase in dispersion bonding and partly due entropy, that is due to the fact that the structure becomes less hydrophilic and partitions more readily from the aqueous phase to the keratin phase which requires less structural organization.

In many shampoos it has become practice to use cationic surfactants or polymers in an anionic shampoo system. The use of a small amount of a cationic ingredient in the presence of a large excess of anionic surfactant results in charge neutralization by the anionic surfactant forming a cationic–anionic complex which is emulsified by the anionic surfactant. These interactions are described in more detail in the next

section for Polyquaternium-10. In effect the cationic (monofunctional or polymer) is converted into a tightly bound neutral salt species (cationic–anionic complex) which is essentially a neutral hydrophobic ingredient. Therefore, in an anionic shampoo system which always has an excess of anionic surfactant, substantivity to hair depends on hydrophobic interactions and entropy rather than a charge–charge interaction. This interaction is entirely different from a cationic conditioner system. These different interactions are described in more detail in the next section under the title of *Cationic Polymer–Surfactant Complexes*. Approximate structural formulas for three cationic polymers that have been used in hair care applications are described in Table 8.2.

8.4.1 Interactions of Quaternized Cellulosic Polymers with Hair

8.4.1.1 Polymer JR (Polyquaternium-10 Formerly Quaternium-19)

Polymer JR has been used in many different commercial hair products as a conditioning ingredient, including several different conditioning shampoos. Polymer JR has a relatively low charge density 670 [31], and a high density of polar groups (hydroxyl), see Table 8.2. Charge density is the residue molecular weight per unit of positive charge. This type of polymer has been studied in three different molecular weight versions – 250,000, 400,000, and 600,000 – in several excellent publications by Faucher, Goddard, and Hannah [23, 25, 31–33].

The chemical structure for polymer JR in Table 8.2 approximates the structure of this polymer and is based on information in the CTFA cosmetic ingredient dictionary [34] and the charge density value of approximately 670 [33]. Note that the positions and numbers of ethoxamer units may vary for this structure, as does the position of the hydroxypropyl quaternary grouping. Polymer JR has been used in several different commercial hair products as a conditioning ingredient, including several different conditioning shampoos.

8.4.1.2 Adsorption and Absorption to Hair

Faucher and Goddard [23] studied the uptake of polymer JR onto bleached and unaltered hair. Their data suggest limited penetration into bleached hair and possibly some penetration into unaltered hair, too, for the lower-molecular-weight portions. At 0.1% polymer concentration, approximately 35 mg polymer per gram hair was sorbed onto bleached hair after 8 days.

After 1 h, 8 mg polymer per gram hair was sorbed (polymer molecular weight: 250,000). A rule of thumb for the uptake of a cationic surfactant (cetyl trimethyl ammonium chloride) onto unaltered hair after 2–5 min reaction time is 1–3 mg

cationic bound per gram of hair. Bleached hair will bind about double that amount, e.g., 4–8 mg per gram (depending on the amount of bleaching). These amounts are essentially surface sorption with limited penetration into the hair.

8.4.1.3 Effect of Molecular Weight

Three different molecular weight versions of Polymer JR (250,000, 400,000, and 600,000) were studied with respect to sorption onto bleached hair [23]. The lowest-molecular-weight species was sorbed fastest and to the greatest extent. The sorption curve for the highest-molecular-weight species shows a rapid uptake followed by leveling, indicating saturation of the hair fiber surface and limited penetration.

8.4.1.4 Effect of Charge

Polymer JR uptake was compared to an analogous uncharged hydroxyethyl cellulose polymer. The uptake of the charged polymer was 50 times that of the uncharged polymer [23].

8.4.1.5 Effect of Concentration

The uptake of polymer JR increased sixfold with concentration, from 0.01% to 1.0% [23]. However, apparent diffusion coefficients from initial slopes indicate a slower diffusion rate with increasing concentration. Faucher and Goddard [23] explain this anomaly by suggesting that a more compact polymer deposits on the hair at the higher concentrations. This may be somewhat analogous to the effects of pH on the activation energy for diffusion of orange II dye into keratin fibers [35]. In this latter situation, the activation energy for diffusion of dye into the fibers increases with decreasing pH where a higher concentration of dye enters the fibers. Apparently, the steeper concentration gradient with decreasing pH increases the energy required for each dye molecule to enter the fibers.

8.4.1.6 Effect of pH

The influence of pH on polymer JR sorption was studied in un-buffered media [23], starting at pH 4, 7, and 10. The largest uptake was at pH 7, with about 15% less polymer sorbed at pH 4 (which can be attributed to a decreasing net negative charge on the fiber surface). However, there is about 30% less polymer pickup at pH 10 than at pH 7, which would not be predicted on the basis of electrostatics or swelling of the hair. Drifting pH caused complications, and the observed differences, although small, await a satisfactory explanation, see *Effects of Salt*.

8.4.1.7 Effects of Salt

Added salt produces a larger effect on the uptake of polymer JR than pH [25]. This salt effect may in fact help to explain the pH effect. The addition of 0.1% sodium chloride decreased pickup by almost two-thirds. This may be attributed to shielding of sorption sites on the hair or competitive inhibition. Although the affinity of sodium ion for hair should be much less than for polymer JR, at this concentration sodium ion has more than 20 times the cationic charge concentration relative to polymer JR.

Other salts, such as lanthanum and calcium, had an even greater effect in decreasing polymer pickup. Trivalent ions (lanthanum, aluminum, and iron) had the largest effect, followed by divalent ions (calcium and ferrous iron). Monovalent ions showed the least effect. Faucher et al. [25] suggested the analogy to hair of a strong acid ion exchange resin and postulated that the decrease in polymer uptake by inorganic cations is due to competitive inhibition.

8.4.1.8 Effect of Hair Damage

Most of the studies with polymer JR employed bleached hair. Bleached hair has a higher concentration of negative sites at and near the fiber surface to attract and bind cations. Bleached hair is also more porous than chemically unaltered hair. As one might predict, uptake of polymer JR onto unaltered hair was an order of magnitude lower than for bleached hair [25].

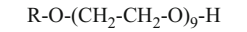
8.4.1.9 Desorption of Polymer JR from Hair

Desorption of polymer JR from hair by distilled water is very slow, and $<15\%$ was removed in a time period of 30 min [25, 32]. Sodium dodecyl sulfate (SDS at 0.1 M) solution, analogous to a shampoo, was more effective, removing more than 50% of the polymer in 1 min and nearly 70% in 30 min. However, a small amount of strongly bound polymer was still attached to the hair after SDS treatment [32]. Attempts to remove this strongly bound polymer by multiple treatments with SDS were not examined.

Salts were also found to be effective in removing a portion of the polymer, and trivalent salts were more effective than divalent, which were more effective than monovalent. However, even after 1 week in 0.1 M lanthanum nitrate solution (La^{+++}), approximately 40% of the polymer was still bound to the hair [25]. Most of these results were on bleached hair, but desorption experiments on chemically unaltered hair indicate related behavior.

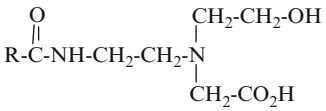
8.4.1.10 Effect of Surfactants on the Sorption of Polymer JR

All surfactants that have been examined, whether neutral, anionic, or cationic, decrease the uptake of polymer JR onto hair [23, 33]. Pareth-15-9, a nonionic surfactant, exhibited the smallest effect in decreasing the uptake of Polymer JR. Faucher and Goddard [23] attribute this to the relatively low affinity of this surfactant for both keratin and the polymer.



Pareth-15-9 (R = C_{11} to C_{15})

Cocoamphoglycinate had a slightly greater effect in decreasing the uptake of JR.



Cocoamphoglycinate

Pickup was greater in the presence of potassium laurate than cocoamphoglycinate. Goddard et al. [33] found a relatively thick, nonuniform deposit in the presence of laurate which they attributed to precipitated calcium laurate (soap) with polymer.

Anionic and cationic surfactants show the largest effect in decreasing polymer JR uptake onto hair. The cationic myristyl benzyl dimethyl ammonium chloride probably functions via competitive inhibition. Anionic surfactants probably function by forming association complexes that neutralize the cationic charge on the polymer most likely forming a negatively charged species in a large excess of anionic surfactant such as in most shampoos. Nevertheless, small amounts of polymer JR were still detected on the hair even in the presence of excessive amounts of anionic surfactant [33].

8.4.2 Cationic Polymer–Surfactant Complexes

Polymers have been shown to form association complexes with surfactants in solution [36–40]. Goddard and Hannah [31] studied the interaction of polymer JR with anionic surfactants such as sodium dodecyl sulfate (SDS) and concluded that this interaction occurs in two stages when anionic detergent is in excess. The first stage involves adsorption of surfactant to the polymer, forming a primary layer that neutralizes the cationic charge on the polymer. A decrease in solubility occurs at this stage, and the new polymer complex is highly surface-active. As the ratio of anionic surfactant to cationic polymer increases, adsorption of a secondary layer results, accompanied by reversal of the net charge of the total polymer complex species. Increased solubility also occurs.

Manuszak-Guerrini et al. [41] expanded on this understanding of the interaction of cationic polymers with anionic surfactants. These scientists confirmed that cationic polymers interacting with anionic surfactants do precipitate at the theoretical charge neutralization ratio. With the polymers studied including Polyquaternium-10 precipitation occurs at concentrations above 0.010% polymer and anionic surfactant. At concentrations <0.010% polymer, a fixed concentration of sodium dodecyl sulfate is required to produce precipitation. The fixed concentration decreases as the charge density of the polymer increases. Further, these scientists demonstrated that the charge density of the polymer is more important than the spacer length for a mono-quaternary derivative. Also these authors demonstrated that the relaxation rate of polymer–surfactant mixed micelle complex is very dependent on the polymer structure.

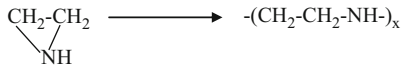
Hannah et al. [32] determined that this type of anionic–cationic complex, formed from 0.1% polymer JR and 1% SDS, does indeed sorb to the hair. Water can remove only some 30% of this JR-SDS complex. SDS and salts are no more effective, leaving some 60% (approximately 0.1 mg complex per gram hair) strongly bound to the hair. Analogous complexes with other cationic polymers have been used for binding or for increasing the substantivity of ingredients to the hair [3, 4].

8.4.3 Polyethyleneimine

Polyethyleneimine (PEI) was used commercially in the 60s and shortly thereafter removed from hair products. However, because of new and improved synthetic techniques, it started making a comeback. Furthermore, several interesting scientific studies have been conducted with this polymer. These studies illustrate some useful principles relevant to the adsorption of cationic polymers to keratin fibers. There are two significant structural differences between PEI and polymer JR:

- PEI has a higher charge density than polymer JR.
- PEI is not quaternized, but is a polyamine.

Polyethyleneimine is formed from the aziridine ethyleneimine, and its chemistry has been reviewed by Woodard [42]. Although PEI is not quaternized, it is highly cationic, since a large number of its amine groups are protonated even near neutral pH. Woodard [42] indicated that at pH 10.5, 4% of the amine nitrogens are protonated; at pH 8, 25%; and at pH 4, 50%. Therefore, PEI would have a charge density of approximately 176 at pH 8, or nearly four times the frequency of cationic sites as polymer JR.



Ethyleneimine Polyethyleneimine

Three different polyethyleneimines have been described with regard to their interactions with human hair; PEI-6 (molecular weight 600); PEI-600 (molecular weight 60,000); and PEI-600E, which is PEI-600 reacted with an almost equivalent amount of ethylene oxide. This reaction with ethylene oxide forms quaternary nitrogen groups and increases the molecular weight to approximately 100,000 [28, 42].

Chow [28] provided evidence for penetration of the lower-molecular-weight PEI-6 into hair. Woodard [42] demonstrated that sorption increases with concentration and with bleaching of hair, similar to polymer JR. Sorption of PEI-6 was also slightly greater at neutral pH compared with acidic or alkaline pH. However, since the charge density of PEI decreases with increasing pH, this result is not unexpected. This PEI study was conducted in an un-buffered medium.

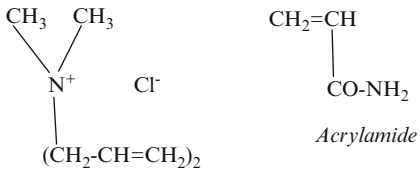
Although a direct comparison has not been made, PEI appears to be even more substantive to hair than polymer JR, probably because of its higher charge density. PEI-600 was sorbed onto hair and tested for desorption toward a 10% shampoo system. After 30 min, less than 20% of the PEI was removed and only approximately 30% after 6 h [42].

The rate of PEI desorption has also been examined with radiolabeled PEI on the hair, desorbing with unlabeled PEI. Most of the polymer, >60%, could not be removed in 24 h by this procedure [28, 42]. This result is consistent with a slow degree of release of PEI due to multiple ionic binding sites to the hair, because it is difficult to uncouple all of the binding sites simultaneously.

PEI polymers, like polymer JR, also interact with anionic ingredients. PEI polymers have been used for increasing the substantivity of other molecules to hair [3, 4]. PEI was formerly used in one commercial shampoo, but has since been removed, presumably because ethyleneimine monomer has been labeled as a carcinogen.

8.4.4 Polyquaternium-6 and -7 Formerly Quaternium-40 and -41 (Merquats)

Polyquaternium-6 and 7 were originally called Merquat polymers and are another type of cationic polymer used in hair care products [43]. One of these (Polyquaternium-6) is a homopolymer of dimethyldiallylammonium chloride (DMDAAC). Polyquaternium-7 is a copolymer of DMDAAC and acrylamide. Polyquaternium-6 has an average molecular weight of approximately 100,000. Polyquaternium-7 has an average molecular weight of approximately 500,000, although different molecular weights may be obtained from the suppliers. Polyquaternium-7 has been used commercially in several different conditioning shampoos.



Dimethyldiallylammonium chloride

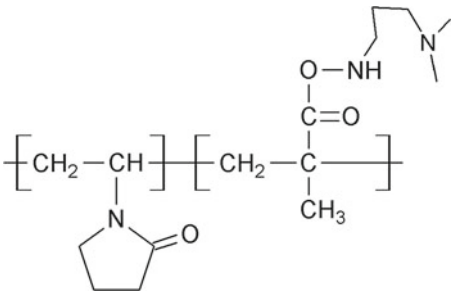
The homopolymer has a charge density of approximately 126, and the copolymer 197. Thus, both of these polymers have a relatively high charge density compared with polymer JR or many other cationic polymers available for use in hair care.

Sykes and Hammes [43] described the adsorption of both of these cationic polymers onto hair from solutions of different amphoteric and anionic surfactants. Analogous to the adsorption of polymer JR, uptake values were greater onto bleached hair than unbleached hair, and greater from amphoteric systems like cocobetaine or cocoamphyglycinate than from anionic surfactants like sodium lauryl sulfate or triethanolammonium lauryl sulfate. The following rationale accounts for these findings. Sodium lauryl sulfate interacts with polymer primarily through an electrostatic interaction. The net result is to neutralize the charge of the polymer and thereby reduce its affinity for keratin. Amphoterics do not neutralize the charge of the cationic polymer as effectively as do anionics. Therefore, cationic polymers demonstrate a greater affinity for keratins in an amphoteric surfactant system than in an anionic surfactant system.

8.4.5 Other Cationic Polymers

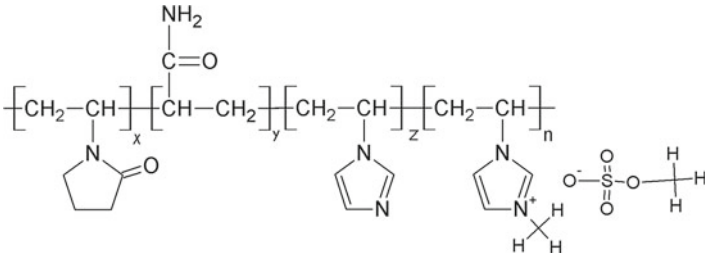
Chemical suppliers to the hair products industry have made a large number of cationic polymers available and many additional cationic polymers have been developed over the past decade. Some of these polymers are carbohydrate derived such as polyquaternium-4 (a grafted copolymer with a cellulosic backbone and quaternary ammonium groups attached through the diallyl dimethyl ammonium chloride moiety; see the section on mousses and Polyquaternium 6 [44]); cationic guar gums such as Guar hydroxypropyl trimonium chloride for example, Jaguar C-13-S or Guar C-261; Ucare polymer LR, a lower-charge-density cationic cellulose derivative of polymer JR; copolymer 845 (PVP/dimethyl aminoethyl methacrylate copolymer derivative of polyquaternium-11, but of lower charge density); copolymers of vinyl imidazole and vinyl pyrrolidone of varying charge density called Luviquats; and even quaternized and amino silicone polymers and copolymers of varying charge density. For additional details on some of these "older" cationic polymers, see the article by Idson and Lee [45]. PVP/DMAPA (vinyl pyrolidone, dmethylaminopropylacrylamide copolymer) has also been

synthesized and through one study provided indications of thermal protective effects against hair damage [46].



PVP/DMAPA acrylates copolymer

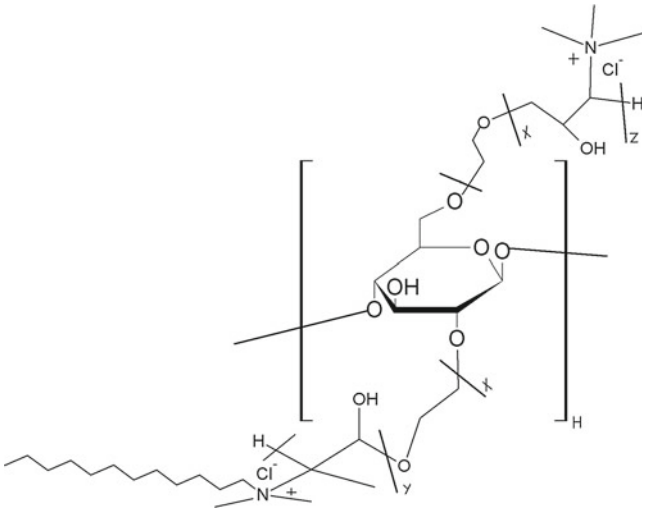
Some additional more recently developed cationic polymers contain three and sometimes four monomeric groups such as Polyquaternium-55 (consisting of copolymers of vinyl pyrollidone, dimethylaminopropyl methacrylamide and methacryloylaminopropyl lauryldimmonium chloride provided by ISP), or Polyquaternium-53 by Nalco (copolymers of acrylic acid, acrylamide and methacrylamidopropyltrimonium chloride) or Polyquaternium-48 by Goo Co. (a betaine, quat polymer consisting of methacryloyl ethyl betaine, 2-hydroxyethyl methacrylate and methacryloyl ethyl trimethyl ammonium chloride) and Polyquaternium-45 (methacrylamide, methacrylamido propyl trimonium and methacryloylethyl trimethyl ammonium chloride) sold by Rohn and Rohm and Haas and an interesting Silicone Quaternium 18 (linear cationic amino silicone block co polymer) and Polyquaternium-68 with the trade name of Luviquat Supreme by BASF. This latter cationic styling polymer contains four different monomeric units consisting of N-vinyl pyrilidone, methacrylamide, vinyl imidazole and vinyl imidazole quaternized with methyl sulfate. The four different monomeric units of this polymer are shown below.



Polyquaternium-68

Some other cationic polymers that should prove to be useful are: Polyquaternium 65 that is based on copolymerizing 2-methacryloyloxy ethyl phosphorylcholine with other momoners, Polyquaternium 69 (trade name Aqua Style 300) by ISP is a copolymer of vinyl caprolactam, vinyl pyrolidone, N-3-(dimethyl amino propyl)-methacrylamide and 3-(methacryloyl-amino) propyl-lauryl-dimethylammonium

chloride and has been used in hair styling gels. Polyquaternium 86 has also found use in hair styling gels and is a composed of four monomers: vinyl pyrolidone, vinyl imidazole, vinyl imidazole quaternized with methyl chloride and methacrylic acid. Polyquaternium 67 is an interesting structure composed of hydroxyethyl cellulose that is quaternized and polymerized with two different quaternary groups. One is n-propyl-2-hydroxy-3-trimethyl ammonium units and the second quaternary group is n-propyl-2-hydroxy-3-dimethyl dodecyl ammonium units.



Polyquaternium-67

8.5 Other Polymers

8.5.1 Polypeptides and Proteins

Polymeric collagen peptides should be somewhat substantive to hair, since they contain multiple ionic and polar sites for bonding, in addition to offering large molecular surfaces with many sites for Van der Waals attachment. Methionine, tyrosine [47], and tryptophan [48] are amino acids or monomeric species of proteins that have been shown to sorb onto hair from aqueous solution. Collagen-derived polypeptides, or polymers of amino acids, have also been shown to have an affinity for hair [49–51]. One would predict that these should be more substantive to hair than their amino acid monomers.

Uptake of this type of species by hair has been shown to increase with either increasing hair damage or increasing polypeptide concentration. An average molecular weight (M_n) of about 1,000 provides optimum pickup, which decreases with higher molecular weight [52] suggesting that diffusion into hair is involved.

Bleaching produces an increase in uptake at neutral pH, whereas thioglycolate-treated hair sorbs more polypeptide at alkaline pH, as does unaltered hair [48]. Bleaching should lower the isoionic point of hair more than thioglycolate, producing more swelling at neutral pH and additional anionic sites to bind polypeptides. Penetration of polypeptide mixtures into hair has been shown by Cooperman and Johnson [51] and is described earlier in this chapter.

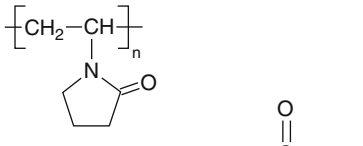
The desorptive action of surfactants and salts on polypeptides already sorbed to hair has not been examined as fully as for polymer JR. On the basis of theory, one would not expect collagen-derived polypeptides to be as substantive to hair as high-charge-density cationic polymers such as Merquats [43] or Luviquat FC 905 [53].

8.5.2 *Neutral and Anionic Polymers*

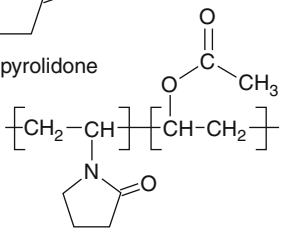
The low isoelectric point of hair, near pH 3.6 [24], suggests that the net charge on the hair fiber surface is negative in the presence of most hair care products (at any pH above the isoelectric point). Table 8.3 describes structural formulas for some of the neutral and anionic polymers that have been used in hair products.

These structures and the isoelectric point of hair suggest that the primary binding of these molecules to hair is by polar and Van der Waals interactions. Since shampooing is in an aqueous system, and water is a good hydrogen bond breaking

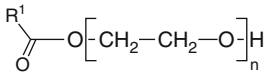
Table 8.3 Some neutral and anionic polymers used in hair products



Polyvinyl pyrolidone



Copolymer of PVP & vinyl acetate



An ethoxylated ester polymer

agent, the principal binding to resist shampooing for this kind of structure comes from Van der Waals attractive forces. Therefore, anionic and neutral polymers are not highly substantive to hair. Therefore, they have been used in applications where their ease of removal by shampoos is almost as important as their adhesional and film properties.

8.5.3 Some Newer Polymer Types for Hair Care

A few block copolymers have been described in the scientific literature for hair care products [54] as well as in patents. These would seem to provide an excellent new type of polymer to provide unique properties for hair products. Fractal polymers or dendrimers, which are large molecules with regular branching, would also appear to be another new area to offer promising new molecules for hair care formulation [55]. Dendrimers are produced by stepwise synthesis in which branches are linked in stages. One example of such a structure is FPEC (fractal poly-epsilon caprolactam) which has been touted to provide enhanced cleaning efficacy at very low concentrations in surfactant solution [55]. Silicone Quaternium 18 (linear cationic amino silicone) is another interesting relatively block co-polymer used in hair care products.

8.5.4 Nanochemistry, Nanoparticles and Hair Care Cosmetics

The area of nanogels and the generation and use of nanoparticles in hair cosmetics is an area that is beginning to receive attention. Nanogels of polyacrylamide and polyacrylic acid have been created and shown to be capable of encapsulating molecules [56]. These have been suggested to offer the slow release of fragrances and the potential for improved release of active ingredients such as antidandruff agents, etc. In addition, a symposium was conducted in 2006 in which one of the major topics was nanochemistry for cosmetics. Therefore, this subject is one of increasing interest yet is in its technological and applied infancy in our field.

8.6 Hair Fixatives

8.6.1 Hair Sprays

The Liquinet Corporation in Chicago introduced aerosol hair sprays into the marketplace in 1949 [57]. Hair sprays have enjoyed considerable commercial success for several decades. However, hair spray sales peaked during 1969 and

began to decline owing to public acceptance of more natural hairstyles not requiring hair fixatives.

In the early to mid 1970s, hair spray sales declined even further because of environmental pressures to restrict the use of fluorocarbons in aerosol products. The large drop in hair spray sales occurred in 1975, after Roland and Molina theorized how fluorocarbons deplete the ozone layer in the stratosphere. As indicated in the introductory section to this chapter, there has been a great deal of research concerned with lowering VOC's in hair care products, and in particular for hair sprays. Furthermore, the California (CARB) regulations outlined in the introduction are the driving force behind these efforts.

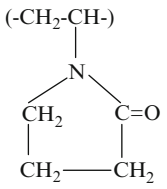
Three types of hair sprays are being produced today: pump hair sprays, hydrocarbon or dimethyl ether aerosols, and carbon dioxide aerosols. The first two of these products account for the major sales for this type of product. Hydrocarbon aerosol hair sprays contain an alcohol-hydrocarbon solvent-propellant system, a synthetic polymeric resin, a base to neutralize the resin if it is a carboxylic acid-containing resin, plasticizer(s), fragrance and, in some cases, surfactant(s)to improve the spreading characteristics of the polymer. Most of the new low VOC aerosol hair sprays contain alcohol-water as the solvent system and dimethyl ether as the propellant. Together the alcohol-dimethyl ether content must be below 55%. For cost considerations, dimethyl ether is a useful propellant, although Hydrofluorocarbon 152-A is exempt as a VOC and provides acceptable, but expensive formulations with most resins including previously used resins [58]. In several counties, there are no VOC limits so hydrocarbon-alcohol systems with virtually no water in these systems can be formulated and sold.

The new low VOC systems with high water content for many of today's "older" resins provide too high a viscosity for spraying. As a result, newer, low molecular weight versions of some of these resins or totally new resins are being touted for the low VOC solvent-propellant systems [59]. For example, Polyurethane-1 (Luviset PUR. a polyesterdiol-dimethylol propionic acid caped with diisocyanate-amine ends and 100% neutralized with AMP) is useful. A lower molecular version of National Starch's Amphomer LV-71 consisting of (octylacrylamide/acrylates/butylaminoethyl methacrylate copolymer) can be used in low VOC systems, but other newer resins are even more effective for low VOC products [60].

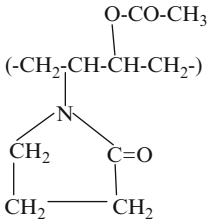
Other useful polymers are DynamX from National Starch (polyurethane-14 AMP acrylates copolymer), Aquaflex FX-64 (isobutylene/ethylmaleimide/hydroxyethylmaleimide copolymer, see Table 8.4) and Allianz LT-120 (acrylates/C1-2 succinates/hydroxyacrylates copolymer) from ISP, Luviset PUR and Polyquaternium 68 both from BASF. The structure of Polyquaternium-68 is described above under cationic polymers.

Improved dispensing systems to handle the new formulations are also useful [58] and are generally recommended with some of the formulations offered by the leading resin suppliers cited in the previous paragraph. Sometimes single polymers show deficiencies (performance or cost) in low VOC systems and mixtures of polymers are sometimes employed to overcome these deficiencies [61]. Normally, higher concentrations (about 30% more) of the lower molecular weight polymers

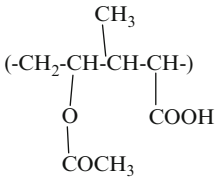
Table 8.4 Some resins used in hair sprays (see text and [1, 58–68] for newer polymers)



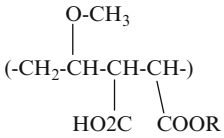
Polyvinylpyrrolidone (PVP)



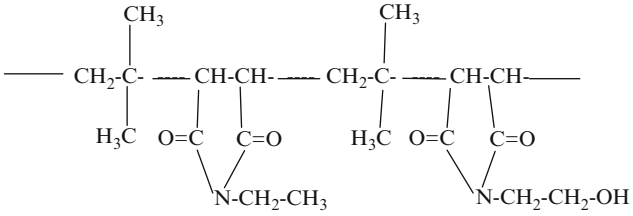
Copolymer of PVP-vinylacetate



Copolymer of vinylacetate and crotonic acid



Copolymer of methyl vinyl ether and a half ester of maleic anhydride



Copolymer of isobutylene, ethyl maleimide and hydroxy ethyl maleimide (Aquaflex FX-64)

must be used to provide equivalent holding power to the higher molecular weight resins. Because of the high water content in the new low VOC systems low levels of corrosion inhibitors such as sodium benzoate or cyclohexylamine are often used, but usually at low concentrations (about 0.1–0.2%).

Pump sprays are very similar to aerosol sprays and consist of solvent(s), a synthetic polymeric resin, a base to neutralize the resin (for carboxylic acid-containing resins), plasticizer(s), and in some cases a surfactant and a fragrance. For the low VOC pump systems, ethanol-water is the preferred solvent.

The resins of all hairsprays are usually synthetic polymers and are the primary ingredient that determines the holding properties of the hair fixative product. Nevertheless, considerable control over the properties of the ionic resins may be achieved by altering the spray characteristics of the product. The degree of neutralization and the type of neutralizer, plasticizer, or type of surfactant employed are also important to the properties of the hair fixative.

Set holding under conditions of changing humidity (especially changes to a higher humidity) is critical to hair spray performance. At the same time, the hair spray fixative system must also be capable of being washed out of the hair by an aqueous detergent system. Thus careful balance of these properties is required to ensure good set stability at high humidity with good washout characteristics.

Synthetic polymeric resins selected for hair spray use are generally anionic or neutral resins rather than cationic to help ensure good washout characteristics. Prior to development of synthetic polymers with a wide range of properties, "hair lacquers" were generally alcoholic solutions of benzoin, rosin, or shellac [62]. These products provided excellent style retention; however, they were difficult to wash out of hair. In the early 1950s, polyvinyl pyrrolidone (PVP) was introduced as a hair-setting agent. This polymer permitted moderate set properties with good washout characteristics. A few years after the introduction of PVP, even better hair setting resins were developed.

Hair sprays, setting lotions, and mousses are related in the sense that each of these products applies a resinous material to the hair and helps to maintain style retention by enhancing interfiber interactions. If the hair is not combed after the resin has set (after the solvent evaporates), rigid contact sites of resin are formed between fibers, analogous to strip welding (Figs. 8.1 and 8.2). This type of interfiber bonding provides the mechanism for set retention of a hair spray.

When the product is applied to wet hair and the hair is set and combed, after the solvent evaporates (as for styling lotions and mousses), the deposited polymer still influences the hair assembly character, by increasing the interfiber forces, but not as

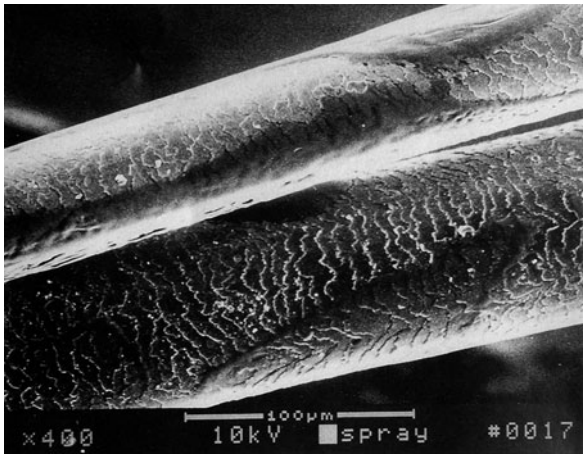


Fig. 8.1 Two hair fibers bonded together with hair spray

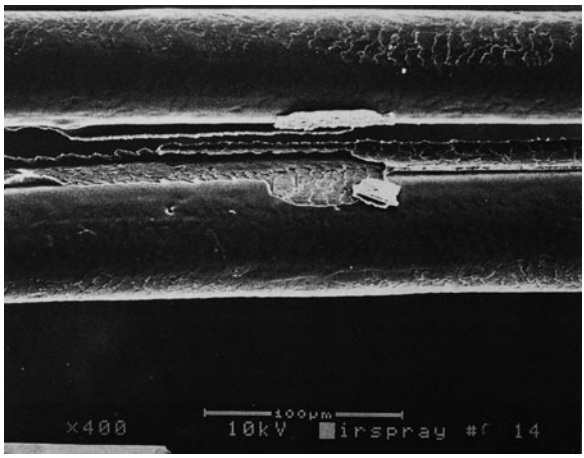


Fig. 8.2 Two hair fibers bonded with a hair spray where the resin is beginning to flake

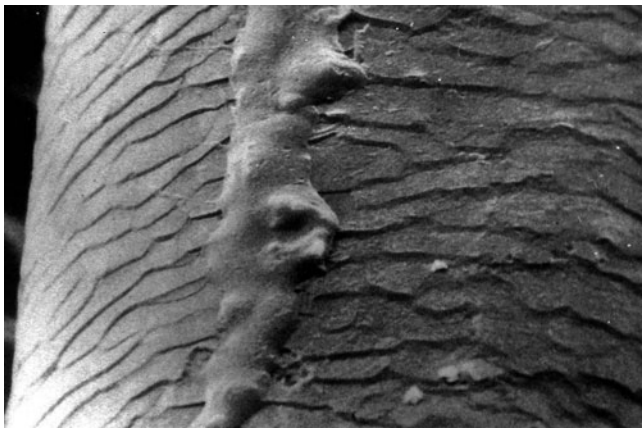


Fig. 8.3 Setting lotion deposit on hair surface

much through rigid interfiber contacts (Fig. 8.3). Many different types of synthetic polymers have been introduced into the marketplace for hair spray use. Chemical structures for three functional and popular types of resins in use today are described in Table 8.4. The polyvinyl pyrrolidone-type resins are usually copolymers of polyvinyl pyrrolidone and vinyl acetate (PVP-VA). These copolymers are more functional than PVP itself, although PVP is widely used in setting lotions and in cheaper hair sprays. A second system widely used for several years is a copolymer of vinyl acetate and crotonic acid. This resin is generally superior to the PVP type resins for hair spray use. Another very functional and popular hair spray resins in retail sale today is the ethyl ester of the copolymer of polyvinyl methyl ether and maleic anhydride (Table 8.4). This product is difficult to use in a low VOC high water

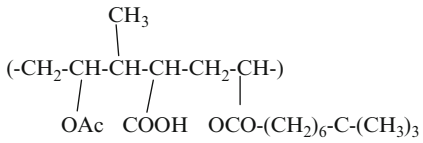
system, even with lower molecular weight modifications. The butyl ester of this copolymer has also been used and is generally superior to the ethyl ester for style retention; however, because of some limitations in fragrance selection for the butyl ester, the ethyl ester has been the most frequently used derivative of this copolymer.

Other, more structurally complex resins, that are highly functional, and in use today are this copolymer of three monomers (vinyl acetate, crotonic acid, and vinyl neodecanoate), and a polymer formed from octylacrylamide, t-butylaminoethyl methacrylate, and two or more monomers consisting of acrylic acid, methacrylic acid, or their simple esters (Table 8.5). This type of polymer provides a low molecular weight version acceptable in low VOC systems; however it is very expensive when used at 30% higher concentration for optimal holding power.

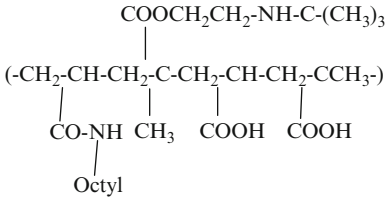
The solvents in pump sprays are limited to alcohol-water mixtures and are therefore not as complex as the solvent-propellant mixtures of aerosols. Generally, ethyl alcohol is the primary solvent, and water the secondary solvent. In some cases, small quantities of propanols or even glycols are used. The solvent and of course the pump spray system largely determine the spray characteristics of a given product which are very important to the functional character of the product [58]. The solvent-propellant systems of today's hydrocarbon aerosol hair sprays used outside the US generally consist of alcohol combined with hydrocarbons such as isobutene, butane or propane and virtually no water. For low VOC systems, dimethyl ether is a useful propellant and acetone may be used as high as 10% and is useful because it is not considered a VOC.

For additional details on aerosol propellants for hair sprays see the previous discussion on VOC propellants and the article by Root [57]. The solvent-propellant in both aerosol and pump sprays contain the VOC and present the apparent

Table 8.5 Two structurally complex, but effective hair spray polymers



Simplified structure for copolymer of vinyl acetate, crotonic acid, and vinyl neodecanoate



Simplified structure for copolymer of octylacrylamide, t-butylaminoethyl methacrylate, acrylic acid (or ester), and methacrylic acid (or esters)

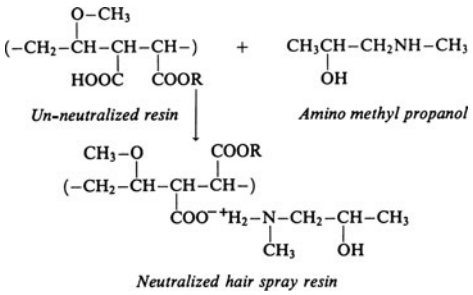


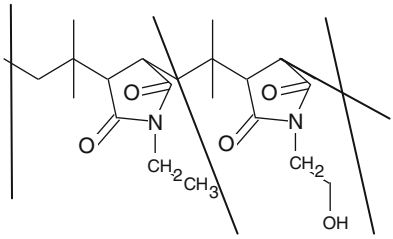
Fig. 8.4 Neutralization of a hair spray resin

environmental problem. As stated, the CARB regulations for 1999 of 55% VOC present the target that has stimulated research and development in this area.

The ability of the resin to spread over the hair surface is largely a function of the resin and is determined by its surface tension and the viscosity of the system. Nevertheless, spreading characteristics of resins can often be improved by adding surfactants [69]. Nonionic or cationic surfactants are generally preferable to anionics for this purpose.

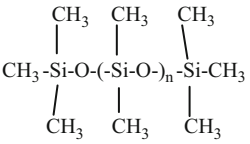
For resins containing carboxylic acid groups, the type of base used to neutralize the resin [69], and the degree of neutralization (see Fig. 8.4) are adjusted to provide optimum film properties and solubility. Organic bases such as aminomethyl propanol, triisopropanol amine or aminomethyl propanediol are generally preferable to inorganic bases as hair spray resin neutralizers.

The structures in Table 8.5 are simplified descriptions of these copolymers and are provided primarily to illustrate the monomers forming the basic structure of some of these polymers. Some of the newer resins used in low VOC hairsprays and other fixative products have already been described in the section on cationic polymers. Others include Aquaflex FX-64 from ISP which is Isobutyhlene/ethylmaleimide/hydroxyethylmaleimide and is highly compatible with water and has been adapted for hair sprays. This structure is shown below. A very novel one from ISP based on Vinyl acetate/butylMaleate/Isobornyl Acrylate copolymer has also found some use in hair sprays as a fixative polymer.

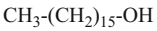


Isobutylene/ethylmaleimide/hydroxyethylmaleimide

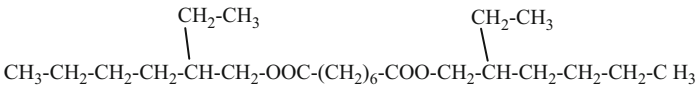
Plasticizers such as dimethicone, cetyl alcohol, dioctyl sebacate, or related ingredients are often added to provide more flexible, less brittle films to minimize flaking and thus to maximize luster and set holding.



Dimethicone



Cetyl alcohol



Dioctyl sebacate

Figure 8.2 illustrates two hair fibers with hair spray resin as the resin begins to flake from the fibers. Plasticizers as above can minimize flaking of resinous products used in hair styling products.

8.6.2 Some Hair Fixative Formulations

These are hair spray concentrates and represent 85% of the total product. The concentrates will be diluted with 15% A-46 Propellant (isobutane and propane) to obtain an acceptable pressure. The spray character will be adjusted with the appropriate valve system. These hair sprays contain 80% VOC and meet the requirements outside of California (Table 8.6).

Table 8.6 Aerosol hair spray concentrates for 80% VOC hair sprays

Ingredient	Holding power		
	Regular (%)	Extra (%)	Super (%)
Octylacrylamide acrylates			
Butylaminoethyl methacrylate	1.5	2.0	3.0
Aminomethylpropanol (AMP)	0.23	0.3	0.4
Glycerine	0.4	0.4	0.4
Dimethicone Copolyol (SF-193)	0.15	0.2	0.3
Octadecyltrimethylammonium			
Chloride 0.06	0.06	0.06	
Fragrance	0.15–0.5	0.15–0.5	0.15–0.5
Alcohol	q.s.	q.s.	q.s.
Water (deionized)	22.5	22	21
Total formula%	85%	85%	85%

8.6.2.1 Hair Spray Making Procedure

Add the alcohol or alcohol and water into the main mixing tank and begin stirring. Add the resin and stir until a clear solution is obtained. Adjust the pH with AMP to 8.5. Add the glycerine, the silicone, the quat and perfume with stirring. Add the water with stirring and when a clear uniform solution is obtained transfer the concentrate to the aerosol filling line for filling and pressurizing (Tables 8.7 and 8.8).

Table 8.7 Examples of aerosol hair sprays that meet the 55% VOC standard

Ingredient	% concentration (extra hold)	[63]	[64]
Polyurethane-1 (Luviset P.U.R.)	4.5		
DynamX		17.85	
Allianz LT-120			12.77
AMP-95			1.0
Ammonium hydroxide			0.25
Alcohol	29.5	17.54	27.0
Water	39.9	31.41	23.7
Dimethyl ether	25	33	28
Dimethicone copolyol	0.2	0.5	
Fragrance	0.2		
Sodium benzoate	0.1		
Cyclohexylamine	0.1		
Triethyl citrate		0.15	
MEA Borate/MIPA borate			0.25
Propellant 152 A			7.0

Table 8.8 Pump hair spray formulations

Ingredient	80% VOC compliant	55% VOC compliant	
		[65]	[66]
Alcohol	79.2	54.18	51.36
DynamX		3.28	14.58
Balance 47		5.10	
Triethyl citrate		0.1	0.15
AMP-isostearoly hydrolyzed wheat protein			0.1
AMP-95		1.2	
Cropeptide W			0.05
Octylacrylamide/acrylates			
Butylaminoethyl methacrylate copolymer	4.5		
Cyclopentasiloxane		0.2	
Diisobuty ladipate	0.05	0.05	
Silsoft A-843	0.05	0.05	
Fragrance	0.3	0.1	
Panthenol		0.1	
Uvinul MS-40		0.05	
Water	15.5	33.59	33.76

The above products are made by the same procedure as for the aerosol hair spray, except no propellant is used and the above represents 100% of the formula. A spritz product can be made from the above formulas by proportioning all ingredients except solvent by about 150%. The 55% VOC product is satisfactory, but not as acceptable as the 80% VOC product primarily because of the slower drying time. Combinations of resins and tailored spray systems may be used to improve this system further.

8.6.3 Mousses

Mousses are related to both hairsprays and setting lotions. Their formulations are generally more complex sometimes consisting of two or more polymeric resins and additives in a water-hydrocarbon (solvent-propellant) system similar to shaving creams. As indicated in the introduction, the CARB standard for January 1, 1994 for mousse hair products was 16% but has been lowered to a maximum of 6% VOC by the end of 2002. Therefore 6% VOC is the standard today.

The resins of mousses are generally cationic such as polyquaternium-4 or polyquaternium-11, or cationic and neutral, or cationic and anionic combined or even amphoteric. Polyquaternium-4 contains both hydroxyethyl cellulose and diallyldimethylammonium chloride. This polymer is related to the quaternized hydroxyethyl cellulose polymer depicted in Table 8.2, except the cationic groups are formed from the diallyldimethylammonium chloride moiety attached to the cellulosic backbone. Polyquaternium-11 (quaternium-23 – Gafquat) is a copolymer of vinyl pyrrolidone and dimethylaminoethyl methacrylate quaternized with dimethyl sulfate. This polymer is related to the quaternized copolymer of PVP depicted in Table 8.2. One mousse product in retail sale contains both of these cationic polymers. Others contain one cationic polymer and either a neutral or an anionic resin such as polyvinyl pyrrolidone, vinyl acetate copolymer or a resin such as the butyl ester of polyvinyl methyl ether, maleic anydride copolymer. Polyquaternium-68 is a newer resin that has been recommended for use in styling and conditioning mousses. Its structure is described in the section on polycationic polymers.

Surfactants and oils are also present in most mousse formulations. Surfactants function to lower the surface tension to help spread the polymer film over the hair surface and to support the foam character of the product. Mousses are added to wet hair. They are combed through the hair without rinsing, to distribute the product throughout the hair. The hair is then styled and dried. Mousses improve wet manageability by lowering combing forces and they enhance body and style retention (Table 8.9).

With these products, the hair is combed dry, after the solvent has evaporated. Therefore, they cannot provide a large number of rigid contacts as hair sprays do; however, they do enhance interfiber attractive forces to provide increased body and improved style retention.

Table 8.9 A styling mousse formulation [67]

Ingredient	Percentage
Part A	
Celquat L-200	1.0
Gafquat 755N	3.5
Balance CR	1.5
AMP Regular	0.09
DC 200 fluid	0.25
Trideceth-12	0.25
Cetyl trimethyl ammonium chloride (CTAC)	0.25
DMDM hydantoin and iodopropynyl butylcarbamate	0.15
Fragrance	q.s.
Water	72.01
Part B	
Propellant A-31	6.0
Propellant 152A	15.0

Making procedure: For Part A, charge the water into the mixing vessel and with stirring add the Celquat until it is completely dispersed. Then add the GAFQUAT and mix until homogeneous. Add the AMP followed by the Balance polymer. When the solution is homogeneous, transfer this concentrate to the aerosol filling line for filling with propellants and pressurizing.

8.6.4 Setting/Styling Lotions and Gels

These products are related to both hair sprays and mousses. They are more similar to mousses, because they are aqueous-based or alcohol-water solvent systems. These products are applied to wet hair or sometimes to dry hair prior to setting as opposed to spraying onto dry hair (Fig. 8.3). Remember, the CARB standard for hair styling gels for January 1, 1994 is 6% VOC and is still in effect.

The resins of styling or setting lotions are usually cationic, for example, polyquaternium-11 (copolymer of vinyl pyrrolidone and dimethylaminoethyl methacrylate quaternized with dimethyl sulfate, similar to the quaternized copolymer of PVP depicted in Table 8.2) – anionic – for example, butyl ester of polyvinylmethyl ether and maleic anhydride – neutral – for example, copolymer of polyvinyl pyrrolidone, vinyl acetate – or even polyvinyl pyrrolidone itself with polyacrylate thickeners. Two more recently developed cationic polymers recommended for styling gels are: Polyquaternium 86 from BASF and Polyquaternium 69 from ISP.

Since the mode of application of these products is similar to the mousse type of product and involves combing the product through wet hair prior to setting and drying and then re-combing the hair after it has dried, these products do not function by forming rigid bonds in the same manner as hair sprays. Nevertheless, these

products do enhance interfiber forces to provide increased hair body and improved style retention (Table 8.10).

Making procedure for the setting lotion formulation:

Charge the alcohol into the mixing vessel. Add the Gafquat resin with stirring and mix until completely dispersed. Add the Solulan, Ammonyx and Emulpor with stirring until the system is homogeneous. Add the water with stirring, and then add the colors and the fragrance.

Making procedure for setting Gel 1 of Table 8.11:

Gel 1: Dissolve the PVP/VA resin in the alcohol and then add about 10% of the formula amount of water. Make a homogeneous solution of the Carbomer in about 80% of the formula amount of water. Deaerate this solution and then add the EDTA and the TEA. In a separate container add, with heating (to about 50°) and stirring, the PEG-40 hydrogenated castor oil to about 10% of the formula amount of water and stirr until it is homogeneous. Add dimethicone copolyol with stirring until it is

Table 8.10 A setting lotion formulation

Ingredient	Percentage
Gafquat 755	5.0
Solulan 98	0.5
Ammonyx 4002	0.1
Emulphor AM-650	0.1
Colors	q.s.
Fragrance	0.2–0.5
Alcohol	35.0
Water (deionizer)	59.06

Table 8.11 Setting/styling gel

Ingredient	Percentage	
	Gel 1	DC Gel [68]
Alcohol	5.0	
PVP/VA 64	2.2	
Triethanolamine	0.6	to pH 7–8
Carbomer 940	0.6	
Carbomer (Carbapol ETD 2020/ Noveon Inc.)		0.43
DMDM Hydantoin		0.1
Water	q.s.	84.77
Dimethicone copolyol	0.3	
Fragrance	0.15–0.4	
PEG-40 hydrogenated castor oil	0.3	
Tetrasodium EDTA	0.1	
Colors	–	
Glycerine		8.0
DC 5-7070 Si Amino Elastomer Emulsion		6.7

Table 8.12 Spray-on gel formulation

Ingredient	Percentage
PVP/VA copolymer	4.0
Isosteareth-20	1.0
DMDM hydantoin	0.7
Octyl salicylate	0.3
Disodium EDTA	0.2
Fragrance	0.2
Water (deionized)	93.6

homogeneous. Cool and add the benzophenone and fragrance to this solution and then slowly mix it into the PVP/VA solution and stir until the system is homogeneous. Add this solution to the Carbomer solution and mix until a clear gel is obtained. Be careful to not aerate the system too much.

Making Procedure for Dow Corning Setting Gel (DC of Table 8.11):

Add the Carbomer to the water and DMDM Hydantoin with stirring. Adjust the pH to between 7 and 8 with triethanolamine. Then add the glycerine and the silicone emulsion with stirring.

The actual products above are in the form of a gel. However, products have appeared in the marketplace that provide hair styling properties like a gel but are not in gel form, but nevertheless, they are called gels. For example, the "spray gel" or "spray-on gel" is such a product (Table 8.12).

Making procedure: Charge the water into the mixing vessel and add the isosteareth-20 with stirring while heating to 50°. Cool to room temperature and add the PVP/VA polymer with stirring. When the system is homogeneous add the remaining ingredients. Polyquaternium-69 and Polyquaternium 86 both described earlier under cationic polymers are newer resins that have found use as styling gel polymers.

8.7 Evaluation of Hair Fixative Products

To develop and evaluate hair sprays, setting products, and mousses, a variety of methods have been developed. Many of the methods described in this section were developed primarily for hair spray formulation and evaluation. Style retention is without question the most important property of hair sprays, therefore several approaches to evaluating hair spray holding power have been described in the literature [70–72]. One novel approach by Ganslaw and Koehler [73] involves measurement of the rate of untwisting of hair swatches treated with hair fixative solution. This method has been called twist retention analysis. It correlates with curl retention and is claimed to allow for more rapid evaluation of data.

Frosch and Vogel [74] developed an approach involving measurement of the force required to break polymer treated hair strands. Another approach, is the

method by Wickett and Sramek [75, 76]. This method involves determining the adhesive strength of hair/hairspray junctions by determining the force required to pull apart two hair fibers joined by a fixed quantity of hair spray. Another approach called dynamic hairspray analysis involves determining the stiffness, rate of drying, duration of tack and maximum tack forces of hair tresses in the form of omega loops [77].

Most of these methods are also used to develop and to evaluate hair setting products and mousses. Very recently, Lang and Sendelback [78] reviewed a large number of test methods for the evaluation of hair spray polymers and products. One of their primary conclusions was, although several interesting and useful methods have been introduced into the scientific literature for fixative polymer evaluation, the well-known curl retention test is still the fastest and most accurate method for obtaining useful information about the holding properties of hair spray polymers.

But, in addition to style or curl retention, several other laboratory tests are helpful to characterize the following properties of hair sprays:

- Product spray characteristics.
- Film properties.

Among the more important spray characteristics are spray rate, spray pattern, and droplet size. Of course, safety considerations related to flammability are also important.

For mousses, measurement of foam properties including foam volume, foam quality, and foam stability is critical to the performance of this type of product. Although such tests have not been described for mousse evaluation, per se, minor modification to shave cream foam tests should provide satisfactory procedures.

Film properties of these products are crucial to performance, and several methods to evaluate film properties of hair spray products have been developed [70, 79, 80]. Erlemann [70] described a variety of methods both subjective and objective to evaluate hair spray films formed on different substrates including metal plates or glass, on flexible foils or tissues, and on hair. Ayer and Thompson [79] describe evaluation of hair spray properties by scanning electron microscopy.

8.8 Silicone Polymers in Hair Care Products

Dimethicones described above in the fixatives section are probably the most widely used silicones in hair care. They are the primary active ingredients of two in one shampoos and of many hair conditioners. As a general rule, the higher the molecular weight the more deposition and conditioning provided by this type of silicone. However, the higher the molecular weight the more difficult the silicone is to formulate into an aqueous composition especially an anionic shampoo system. As a result, optimum effects are generally achieved at a viscosity of 10,000–40,000 cps. Many functionalized silicones have been introduced into the patent literature and some of these into the market place [79–87]. Some examples of these are

aminosilicones, anionic silicones, alkyl-modified siloxysilicates [81] and even silicones containing quaternary groups [88]. As a general rule the dimethicone type silicones without other functionality have proven to be the most widely used to date for many compositions.

Dimethicone copolyols or silicone glycol copolymers have been used as plasticizers for resins and as co-solubilizers in shampoo systems. Because of the high water solubility (affinity for water versus hair) and low total Van der Waal's bond strength, the lower molecular weight copolyols and glycol copolymers are not good conditioning agents for a rinse off hair product. However, Yahagi [87] concluded that high molecular weight dimethicone copolyols with small amounts of copolyol and therefore a low HLB (hydrophile lipophile balance) can deposit onto hair and function as conditioning agents, but they are not as effective as dimethicones. Nanavati and Hami [86] described the adsorption of dimethicones and dimethiconols of higher molecular weight (10,000–64,000 for dimethicones and 220,000–280,000 for dimethiconol gums) onto hair.

Dimethicones formulated into a shampoo can protect the hair against some damaging abrasive actions of combing and brushing [89]. Some silicone polymers containing phenyl groups have high refractive indices (near 1.5) and are reported to enhance the shine of hair fibers. Siloxysilicate polymers containing alkyl groups longer than C12 have been described by Berthiaume and Baum [81] to increase hair body. These same authors describe ester siloxysilicate polymers for conditioning hair, but they are less substantive to hair than alkyl siloxysilicates where the alkyl groups are C 12 or longer.

Gamez-Garcia [90] demonstrated that an aqueous solution of a protein polysiloxane copolymer at 2% could prevent cuticle cracking from thermal cycling, see Chap. 9 for details of this effect. A cystine polysiloxane polymer has been shown by Gamez-Garcia [91] to be capable of re-cementing cuticle scales that have been previously lifted.

Amino functional silicones, on the other hand, have been used in hair conditioners and shampoos for several years to improve hair conditioning. Because of the potential cationic charge on amino functional silicones, it is sometimes mistakenly accepted that all amino silicones are more substantive to hair than dimethicones in all systems. Several years ago we conducted a study among amodimethicones of varying molecular weight (about 1,000–60,000 Da) and charge density. We found that adsorption to hair from an anionic shampoo in an aqueous medium is more a function of molecular weight than charge of the silicone. Consistent with this effect is the fact that the amount of dimethicone adsorbed to hair generally increased with increasing molecular weight. Apparently, for silicone polymers that are emulsified or dispersed in an aqueous medium, because of their low water solubility, entropy is important to the adsorption process.

There is oftentimes more entropy or random structural organization for a silicone molecule to adsorb to a hair fiber surface than to emulsify or disperse it into an aqueous system. To form such a stable emulsion or dispersion requires a great deal of structural organization. Therefore, when the silicone can adsorb with an increase in entropy the process becomes entropy driven. For lower molecular weight

silicones in a neutral medium, charge could be more important and could override entropy-involved factors.

Dimethicone conditioning agents in anionic shampoos are dispersed as large particles generally about 20 μm in diameter. The particle size of the dispersed dimethicone and the dispersing agents are important to the overall conditioning delivered. For example, if one takes a good conditioning dimethicone shampoo and homogenizes it so that the particle size decreases appreciably conditioning is decreased and can be totally eliminated. The stabilizing agents or suspending agents used in the formulation are also important to conditioning. In one of the first patents on dimethicone containing conditioning shampoos the stabilizing agent was claimed to be fatty amide. However, intensive study revealed that the polymeric gum also played a significant role in product stability. Furthermore it has been shown that one can decrease conditioning by simply increasing the amount of polymeric gum stabilizer in the system. Long chain fatty alcohols have also been used as stabilizing agents. These alcohols have also been shown to adsorb onto the hair with the dimethicone.

It is well known that dimethicone polymers formulated into a shampoo system adsorb more readily onto undamaged hair than onto damaged hair and even more readily onto root ends of hair than tip ends. This is because dimethicones are so hydrophobic that the more the hair is damaged, the more hydrophilic the hair surface becomes and the less the hydrophobic silicone adsorbs to it. One way to compensate for this poor affinity that results from increasing hair damage is to use cationic polymeric bridging agents. Some cationic polymers can function as bridging agents, especially on damaged hair by increasing the affinity between the hair and the hydrophobic silicone. This concept is related to the work of Nanavanti and Hami [86], and others, who demonstrated that adsorption and conditioning of dimethicones onto bleached hair can be enhanced by formulation with quaternary ammonium compounds.

The concept of bridging agents in these systems is useful because the quaternary ammonium polymer has both hydrophilic and hydrophobic sites. Therefore it has a higher affinity for the hydrophilic damaged hair fiber surface than the silicone. Thus, the bridging agent creates more binding of silicone to the hair surface in one of two possible ways. It either binds to the hair surface making that surface more receptive to the hydrophobic silicone or it binds to the silicone making the silicone particles more attractive to the hair surface. In either event, more silicone is adsorbed onto the hair surface and conditioning of damaged hair is made more effective. Berthiaume and Jachowicz [92] demonstrated that polydimethyl siloxanes from 50 to 12,500 cSt in aqueous emulsions deposit more readily onto hair that has been pretreated with a cationic polymer (poly-dimethacrylamidopropyltrimethyl ammonium chloride) than onto untreated hair. This one experiment suggests that the cationic polymer likely first deposits onto the hair surface increasing the affinity of the hair for the hydrophobic silicone. One must also keep in mind that a quaternary ammonium polymer (at a low concentration) in an anionic shampoo system (with a high concentration of anionic surfactant) is neutralized and suspended partly by the anionic surfactant. Therefore, it becomes a negatively

charged species, but it still can have a higher affinity for the damaged hair surface than the very hydrophobic silicone.

Similar to cationic polymers, low concentrations of amino silicones in an anionic shampoo are essentially anionic species because of complex formation with the excess anionic surfactant. These complexes helps to explain why the adsorption of amino silicones from an anionic shampoo is largely dependent on molecular weight (sorption increases with molecular weight) rather than on charge density of the amino groups. Sorption is also dependent on the structure of the anionic surfactant employed.

8.9 In-Situ Polymerizations in Hair

With the exception of oxidation hair dyes, in situ polymerizations in hair have been only laboratory and concept curiosities. However, remarkable changes to the chemical [93] and physical properties [94] of the fibers have already been achieved using this technology. In the future, through the combination of science and imagination, some in-situ polymerization hair treatment may end up in the marketplace. The remaining sections of this chapter describe oxidation dyes as in-situ polymerization hair treatments and in-situ vinyl polymerization reactions in human hair.

8.9.1 Oxidation Dye Reactions as In Situ Polymerization Reactions

Although not generally described as such, certain reactions of oxidation hair dyes are examples of in-situ polymerizations in hair. These consist of the oxidation of electron-rich aromatic amine and phenol monomers that condense with each other and perhaps even attach to amino acid residues of hair. The net result, at least with products containing p-phenylenediamine (PPD) and resorcinol, is the formation of polyindophenol-type polymeric pigments [95–97] that render color to the hair. (See the discussion on oxidation hair dyes in Chap. 5 and its references for additional details.)

8.9.2 In-Situ Polymerization of Vinyl Monomers in Hair

Several techniques have been employed for the polymerization of vinyl monomers on and in wool fiber.

- Reduction of the fibers, followed by reaction with vinyl monomer and oxidizing agent in an inert atmosphere [98, 99].

- Radiation grafting [100, 101].
- The Wurlan Process [102] – which is the condensation of diamines and diacid chloride in the presence of wool fiber.

The procedure that has been most thoroughly studied for polymerization into human hair is related to the first procedure above, that is the reduction of the fibers (in an air atmosphere) [103, 104] followed by reaction with vinyl monomer and an oxidizing agent.

8.9.3 Mechanism of Action

Polymerization of a vinyl monomer into human hair is a complicated, multi-step process that may be summarized by the following reaction scheme:

1. Diffusion of reducing agent into the fibers.
2. Nucleophilic cleavage of the sulfur-sulfur bond by reducing agent.
3. Water rinse.
4. Diffusion of oxidizing agent into the fibers.
5. Reaction of reduced hair and oxidizing agent.
6. Diffusion of vinyl monomer into the fibers.
7. Chain-initiating reactions.
8. Chain-propagating reactions.
9. Termination of free radical chains.

Steps 1 through 3

Among the reducing agents that have been employed in this type of process are thioglycolic acid (TGA) [90], bisulfite [79], and tetrakis (hydroxymethyl) phosphonium chloride (THPC) [104]. The critical point in this step is the extent of reduction, since each of these reducing agents provides increasing polymer add-on with increasing time of reduction (Fig. 8.5). Comparison of the TGA system with the bisulfite system shows a faster rate of polymerization with TGA than with bisulfite. This rate difference is consistent with a faster rate of reduction of hair by TGA. Since the reaction of TGA with human hair is diffusion-controlled [105], step 2 is extremely important to the overall kinetic scheme. But, since cleavage of the sulfur-sulfur bond by TGA is faster than diffusion, Step 2 seems of lesser importance to the overall kinetic scheme than Step 1. However, the extent of disulfide fission is a controlling factor in the remaining steps: the diffusion of initiator (oxidizing agent) and monomer into the fibers.

The effect of pH during reduction is very important to both the TGA [103] and the THPC [104] systems. In the case of the TGA system, reduction rate increases with pH, and polymer add-on increases similarly. For the THPC system, pH is also critical, but not for entirely the same reason. According to Jenkins and Wolfram

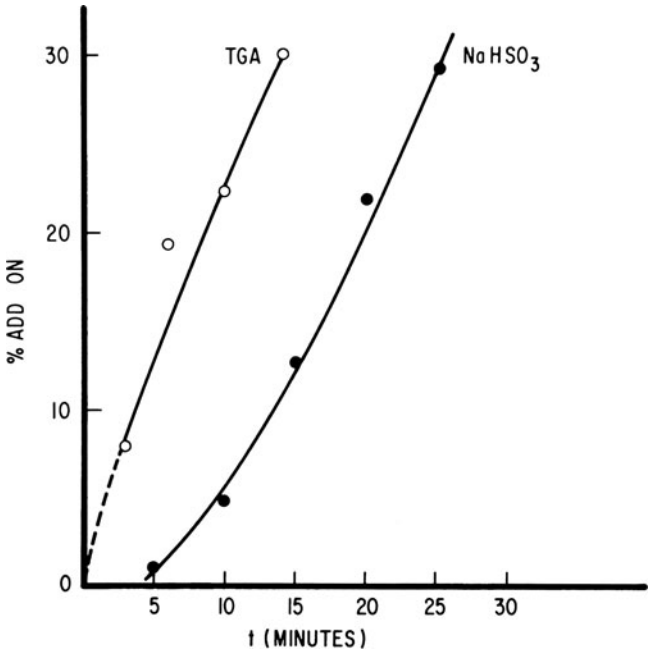


Fig. 8.5 Influence of the reduction step on polymer add-on [103] (Reprinted with permission of the Journal of the Society of Cosmetic Chemists)

[106], THPC dissociates in aqueous solution to Tris (hydroxymethyl) phosphine (THP), and THP is the actual ingredient that reduces the hair.

$$\underset{\text{(THPC)}}{\text{P-(CH}_2\text{-OH)}_4^{+}\text{Cl}^{-}} \longrightarrow \underset{\text{(THP)}}{\text{P-(CH}_2\text{-OH)}_3} + \text{CH}_2\text{O} + \text{HCl}$$

Wolfram [104] has shown that polymer add-on increases with pH of the reducing solution, up to pH 7, where it appears to level. Thus, THPC dissociation and sulfur-sulfur bond cleavage also increase with pH up to 7. The fact that polymer add-on is not higher at pH 9.2 than at 7.0 suggests interference of alkalinity in a subsequent reaction step. The most probable complications are in the chain initiation or propagation steps, since Wolfram indicates that the cysteine-persulfate redox system is optimal in the pH region of 1.5–3.5.

Steps 4 Through 9

Both TGA-hydroperoxide and THPC-persulfate systems show a linear relationship between polymer add-on and the square root of time, (Fig. 8.6) [107]. In both of these systems, the amount of polymer add-on can be influenced by concentration changes in both oxidizing agent and vinyl monomer. Therefore, the diffusion of vinyl monomer and oxidizing agent into the fibers can also be rate

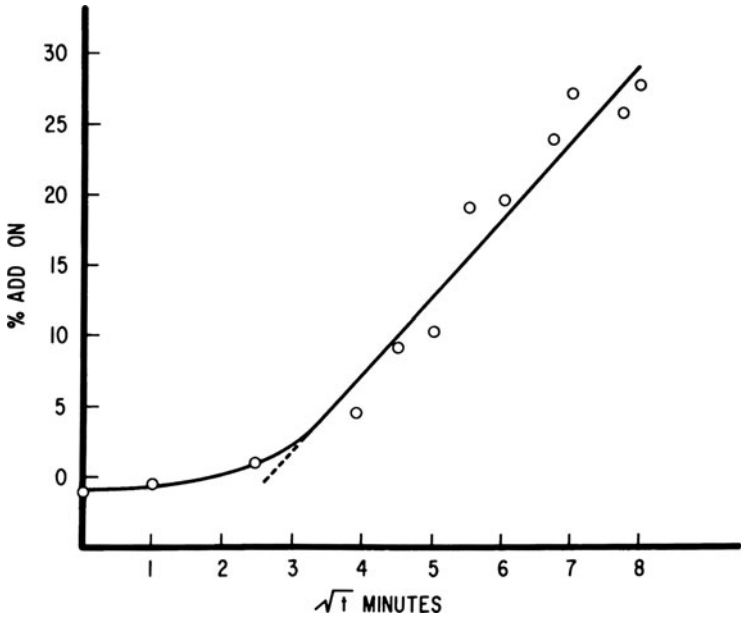


Fig. 8.6 Influence of reaction time (steps 4–9) on polymer add-on [103] (Reprinted with permission of the Journal of the Society of Cosmetic Chemists)

limiting. As a result, any variable that can accelerate diffusion of oxidizing agent and/or vinyl monomer into the fibers is capable of increasing the rate of polymer add-on.

Step 5, the reaction between reduced hair and oxidizing agent, generates the free-radical species that initiates polymerization. For the system of Wolfram [104], this step involves reaction of THP or mercaptan of reduced hair with persulfate. But, for the TGA system, it involves reaction of mercaptan with cumene hydroperoxide.

The remaining reactions, steps 8 and 9, are classical free-radical propagation and termination reactions, summarized by Fig. 8.7. If the chain-initiating radicals are from cysteine residues or other residues of the hair, then the resultant polymer is grafted (i.e., covalently bonded to the hair protein). However, if the chain-initiating radicals are from oxidizing agent or reducing agent, then the polymer, if inside the hair, may become entrapped as it grows.

8.9.4 Solvent System and Its Effect on Polymerization

For the TGA-cumene hydroperoxide system, an ethanol water solvent was employed for monomer and initiator. The data clearly demonstrate maximum

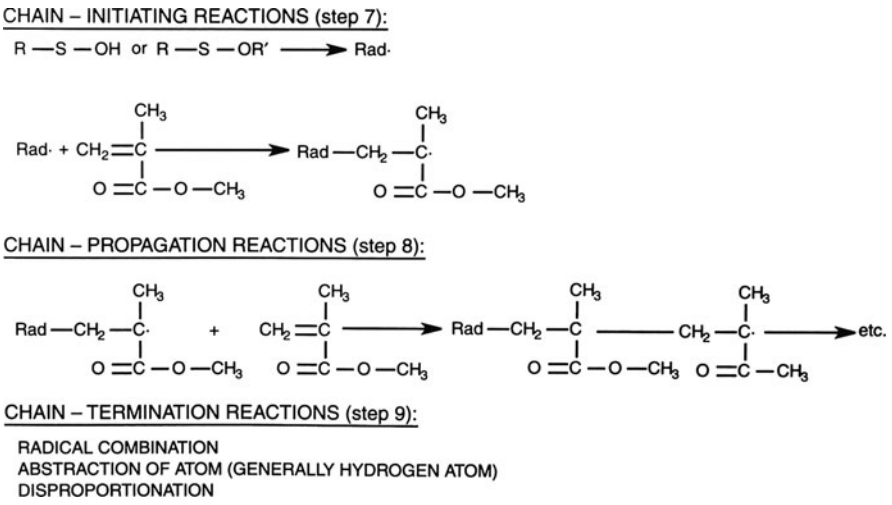


Fig. 8.7 Chain initiation, propagation, and termination steps

Table 8.13 Polymerization into bleached hair with methyl methacrylate [93]

% cystine in hair	% add-on
18.1	12
15.9	18
15.4	21
14.5	25
10.9	38

add-on with larger proportions of water in the system, providing greater hair swelling, consistent with diffusion rate control [101].

8.9.5 Polymerization into Chemically Altered Hair

Bleaching increases the permeability of hair. However, bleaching also decreases the disulfide content, and the disulfide bonds are potential sites to form mercaptan groups, a part of the redox system. Therefore, it was of interest to determine which of these two parameters, permeability or mercaptan content, might contribute more to the rate of polymer add-on. Hair was bleached to varying extents with alkaline hydrogen peroxide and then treated with a bisulfite-cumene-hydroperoxide system, using methyl methacrylate monomer. The data clearly show increasing polymer add-on with decreasing disulfide cross-links (Table 8.13), once again emphasizing the importance of diffusion rate control to this process [103]. Figure 8.8 shows

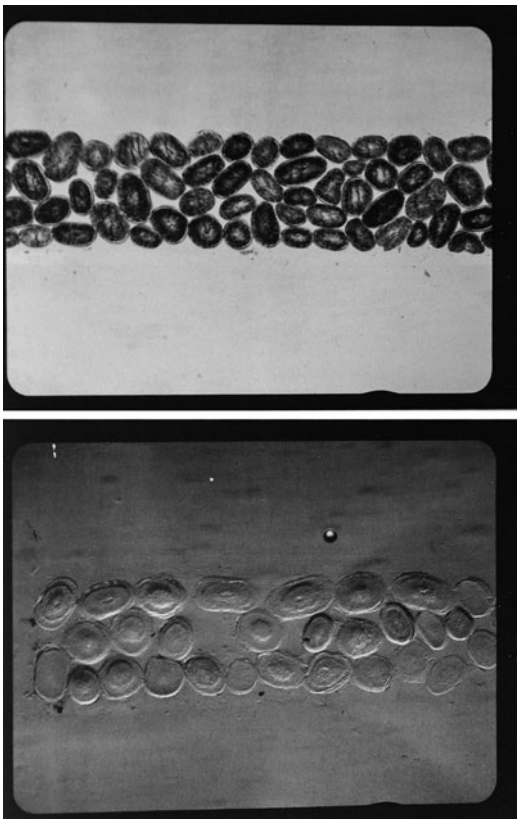


Fig. 8.8 Cross-sections of hair fibers containing two different amounts of polymethyl methacrylate. *Top*: Fibers containing 16% add-on. *Bottom*: Fibers containing more than 100% add-on

cross-sections of polymethyl methacrylate grafted hair fibers with a low add-on (top – 16% add-on) and a high add-on (bottom >100% add-on). Grafting was also carried out on reduced-oxidized hair, that is, hair that was permanent waved to varying extents prior to treatment with the polymerization system [103]. This hair also provided very large add-ons.

8.9.6 Evidence for Polymer in the Hair

Hair after treatment with TGA-cumene hydroperoxide using methyl methacrylate monomer was hydrolyzed, using 5 N hydrochloric acid. Acid hydrolysis dissolved away the keratin from the polymer. Part of the resultant fiber-like residue was dissolved in organic solvents. The solute (in the organic solvents) was shown to be poly methyl methacrylate by refractive index and infrared spectroscopy [101].

Viscosity average molecular weights of this polymer were determined from bleached, permanent waved and chemically unaltered hair and found to be relatively constant near 90,000 Da. This result suggests an average degree of polymerization of approximately 900.

Scanning electron micrographs of the surface of hair fibers treated with the TGA-cumene hydroperoxide system using methyl methacrylate monomer show a thick coating of polymer on the hair fiber surface. However, the fibers still retain repeating irregularities perpendicular to the fiber axis, which correspond to scale edges covered with a thick coating of polymer (Fig. 8.9) [103].

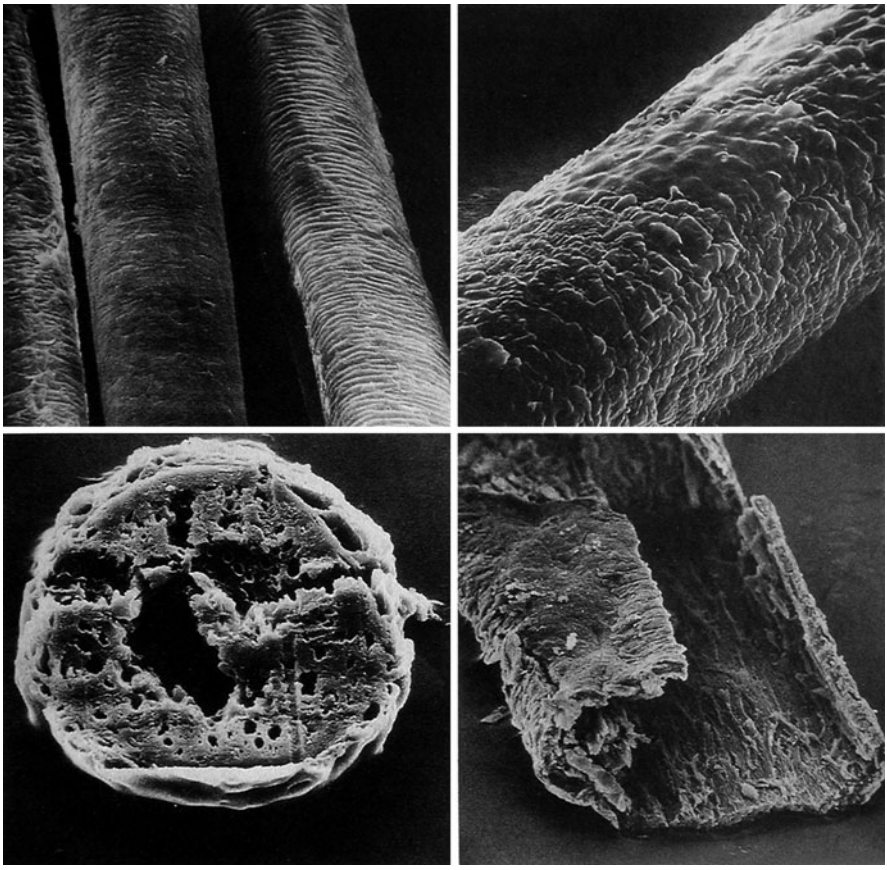


Fig. 8.9 Scanning electron micrographs of PMM-containing hair fibers [103]. *Upper left*: Surface of hair fibers containing 16% PMM add-on. *Upper right*: Surface of hair fibers containing 119% PMM add-on. *Lower left*: Cross section after hydrolysis of hair fibers containing 119% add-on. *Lower right*: End view after hydrolysis of hair containing 16% add-on (Reprinted with permission of the Journal of the Society of Cosmetic Chemists)

Fig. 8.10 Hair fiber containing 119% polymethyl methacrylate reacted with sodium sulfide to remove a large portion of the hair from the polymer [103] (Reprinted with permission of the Journal of the Society of Cosmetic Chemists)

As indicated, fiberlike fragments were isolated from polymethyl methacrylate after hydrolyzing away much of the keratin with 5 N hydrochloric acid. These "synthetic fibers" after hydrolysis were examined in cross section and at the ends. From hair with large amounts of polymer add-on (near 100% weight gain), these "fibers" were almost complete cylinders of porous polymethyl methacrylate threads, whereas hair with lower polymer add-ons (10–20% weight gain) yielded thin-walled hollow cylinders (Fig. 8.9). The fibrous structure illustrated in Fig. 8.10 was obtained after treatment of polymethyl methacrylate containing hair with nearly 100% add-on with sodium sulfide to partially dissolve away much of the hair proteins. Note the hollow cylinder of polymer remaining reminiscent of ring dyed hair. Figure 8.11 depicts additional micrographs illustrating the polymer-hair structures after polymerizing methyl methacrylate onto and into hair (no hydrolysis) with very large add-ons of about 100%. These observations are consistent with diffusion rate control for this in situ vinyl polymerization process.

8.10 Safety Considerations for Polymers

Safety considerations for products containing polymers are often related to the components other than the polymer (monomers, catalysts, etc.) rather than the polymers. The polymers themselves are usually relatively safe ingredients. Protein polymers should be tested for sensitization; however, such problems are not frequent for the types of protein hydrolysates used in hair care. "Pure" synthetic polymers (with no monomer contaminant) are generally mild ingredients of

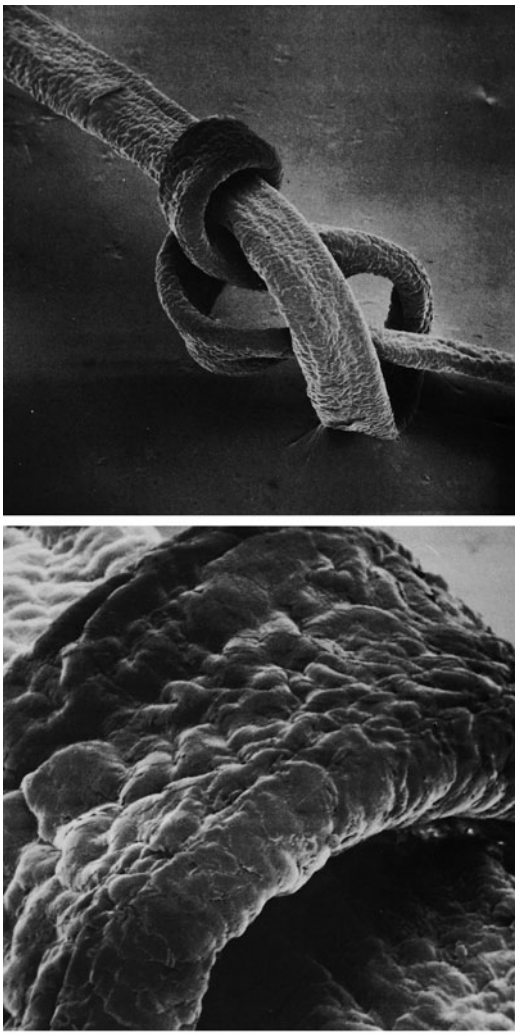


Fig. 8.11 *Top*: A knotted fiber containing more than 100% polymethyl methacrylate. *Bottom*: A close up of the same fiber

relatively low toxicity, one example being polyvinyl pyrrolidone originally used as a blood plasma extender in medicine.

Safety concerns for synthetic polymers are sometimes due to contamination with monomeric impurity. Monomers are sometimes highly toxic such as acrylamide [108], or even carcinogenic such as ethyleneimine [109] or vinyl chloride [110], or highly irritating to skin, such as acrylamide [108] or acrylic acid [108]. Therefore, control of unreacted monomer level can sometimes be critical to the safety performance of synthetic polymers.

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Chapter 9
The Physical Properties of Hair Fibers

Abstract This chapter describes tensile, bending and torsional testing including different parameters of each of these deformations and how these are affected by different types of hair including different types of hair damage. Expanded data sets are included for elastic moduli and other parameters of these deformations. A new section describing the historical development for assessing and measuring hair fiber curvature along with a new method for curvature has been developed and applied to more than 2,400 persons from more than 20 different countries. This method and data are featured in this section. Methods to determine the different dimensions of hair fibers including axial (length and curvature) and transverse dimensions (diameter, cross-sectional area and ellipticity) are described with much expanded data sets. Information on hair fiber friction (both high load and low load friction) and how friction varies with fiber diameter, comb composition and hair damage are included. Mechanical fatiguing, extension cycling and their effects on hair damage including scale lifting are described in the final section on the physical properties of hair fibers.

9.1 Introduction

Since the 4th edition, several important advances have been made in our understanding of the more important physical properties of hair fibers. A new method for hair fiber curvature Segmentation Tree Analysis Method (STAM) classifies this important property into eight different curl types. This method has been applied to more than 2,400 persons from several different countries over the three most important geo-racial groups (linking geography with race) across five continents. This quantization of hair fiber curvature is significant because of the importance of hair fiber curvature to all cosmetic hair assembly properties. As a result, I have attempted to assign hair curvature by STAM to as many parts of this text as feasible.

Additional data on hair diameters, ellipticity, elastic modulus, breaking stress and other important parameters are presented using larger data sets than in previous

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editions. New data on the effects of age and sex on scalp hair diameter are presented. This discussion includes new findings on the effects of the menopause on the scalp hair diameter of females. Variation of fiber diameter and ellipticity along the hair shaft and age effects on cross sectional area, ellipticity, curvature and the scale index have also been added.

New and important findings on torsional and bending properties of damaged hair and the effects of different treatments on these properties have been included. Torsional properties have been under-utilized and are potentially just as important as tensile properties because torsion can reveal damage and prospective repair to the cuticle as well as the cortex, an inherent weakness of tensile testing. Torsional properties are also more sensitive to relative humidity changes or water content in the fibers than tensile properties. Additional evidence has been provided to confirm that tensile properties reside essentially in the cortex and not the cuticle for human hair fibers. Torsional measurements can also detect changes induced by hair spray films and conditioner binding in the cuticle that tensile measurements cannot discern. The relationship between structure and adhesion failure (fracture formation) in different parts of the hair is also presented.

Useful information on how hair is degraded with hot combs and by alkaline hair straighteners has been added in sections dealing with hair damaging treatments. New findings showing the importance of bending stiffness and friction on hair handle or feel is also described in Chap. 10 and a new approach to the assessment of tactile hair properties using a psycho-physiological technique has been offered in the literature.

For the main discussion in this chapter, the physical properties of human hair have been divided into two categories:

Elastic deformations
Other important physical properties

Another important classification that will be referred to routinely is single fiber and fiber assembly properties. Some of the more important single fiber properties described in this chapter are curvature, elastic deformations, friction, cross-sectional area (diameter), ellipticity and cohesive/adhesive forces.

Elastic deformations include stretching (tensile properties, cyclic extension and fatiguing), bending including stiffness or the resistance to bending, and torsion (twisting) and its resistance, rigidity. Hair damage/breakage properties have become of paramount importance to cosmetic science and hair breakage is described in Chap. 10. Tensile testing has been used for decades to assess damage to hair, but tensile testing does not closely simulate damaging/breakage effects from hair grooming.

The density of hair (mass/volume) is considered in this chapter followed by fiber dimensions including diameter, ellipticity, cross-sectional shape, and curvature followed by fiber friction as other important physical properties.

The last section of this chapter deals with fatigue testing, extension cycling and flex abrasion which are becoming more widely used because the former two methods simulate some of the damaging effects of grooming actions and can reveal

damage to the cuticle at a level that tensile testing cannot, while flex abrasion more closely simulates a few of the actions involved in hair breakage.

Several years ago, Robbins and Scott [1] hypothesized that most consumer assessments of hair (properties of fiber assemblies such as combing ease, style retention, flyaway, body, and manageability) may be approximated by algebraic expressions involving the single fiber properties of friction, stiffness, static charge, fiber curvature, weight, diameter, luster, and color. Hough et al. [2] described a somewhat similar analysis of hair body. Robbins and Reich [3] determined empirical relationships between combing ease and the fiber properties of friction, stiffness, fiber curvature, and diameter. This work demonstrated that hair assembly properties can indeed be defined by a few fundamental single fiber properties. Robbins has taken the conclusions from this study and proposed a general hypothesis for hair behavior. This general approach of relating fiber assembly behavior to single fiber properties has been expanded and is the basis for the discussion on consumer assessments in Chap. 10.

9.2 Tensile Extension and Deformations

9.2.1 Definitions and Conditions Important to Tensile Extension

For every "strain" (deformation) of an elastic substance, there is a corresponding "stress" (the tendency to recover its normal condition). The units of stress are force per unit area (F/A). The most common types of strain are stretching or elongation (the ratio of an increase in length to the original length), linear compression (the ratio of a decrease in length to the original length), shear (the ratio of the displacement of one plane relative to an adjacent plane), bending, and torsion [4]. These latter two strains are combinations of the former three. Only stretching, bending, and torsional strains are considered in this chapter. For a summary of stress strain models see the section entitled *Stretching Hair and Stress Strain Models* in Chap. 1.

Each type of stress and strain has a modulus (the ratio of stress to strain) that also has units of F/A. The elastic modulus for stretching is commonly called Young's modulus. The bending modulus is called Young's modulus of bending, and the torsional modulus is called the modulus of rigidity. But, keep in mind that these elastic moduli for stretching, bending and torsion apply to only limited amounts of deformation (small% strains) for hair fibers over the "elastic" region.

Human hair has been referred to as a substrate with only one dimension, "length," suggesting why its tensile properties have been studied more than its other elastic properties. The usual procedure for evaluating the stretching properties of human hair involves stretching a fiber of known length (we usually used 5 cm fibers), at a fixed rate (a convenient rate is 0.25 cm/min) in water, in buffer, or at a fixed relative humidity (approximately 60% RH), near room temperature on an automated instrument such as an Instron Tensile Tester (Fig. 9.1) or a Dia-Stron

Fig. 9.1 A single hair fiber loaded in an Instron tensile tester for load–elongation study

Tensile Module. It is unfortunate that there is no standard test conditions in the cosmetic industry for this widely used procedure.

Tensile properties are whole fiber properties, as opposed to surface properties and evidence is strong that tensile properties are primarily cortical properties and not related to the cuticle. This experimental evidence is described next in this chapter with accepted models described in Chap. 1 that explain stretching and water absorption in terms of the cortex [5] with no cuticle involvement. Wolfram and Lindemann [6] suggested that the cuticle might contribute to the tensile properties, especially in fine hair. However, Scott (personal communication) provided support for the "no cuticle involvement" hypothesis, by evaluating the tensile properties of hair fibers that were abraded under controlled conditions. In no instance could he demonstrate a significant change in tensile properties where only cuticle had been abraded.

Robbins and Crawford [7] published the first experimental evidence that the cortex and not the cuticle is responsible for the tensile properties of human hair by

showing that severe damage to the cuticle only cannot be detected by tensile property evaluation. This work involved selective oxidation of the cuticle with m-diperisophthalic acid and is described in more detail with SEM's in Chap. 5. This oxidative treatment (m-diperisophthalic acid) produces extensive cuticle damage that is detectable microscopically. However, this damage could not be detected by either wet or dry tensile property evaluation. More recently, Persaud and Kamath [8] provided additional evidence that tensile properties are a property of the cortex. These scientists demonstrated that cetyl trimethyl ammonium bromide (CTAB) in the hair can be detected by torsional measurements but not by tensile measurements. Persaud and Kamath concluded that this quaternary surfactant absorbs in the cuticle and strengthens it. They suggested that CTAB does not produce changes in the cortex and therefore could not be detected using tensile measurements.

Additional supporting evidence for the non-cuticle involvement in tensile properties is the fact that wet extension of hair fibers to 30% damages the cuticle [9] yet on relaxation in water, tensile recovery occurs producing virtually identical elongation-recovery curves in a before and after evaluation. This basic elongation-recovery procedure (to 15%, 20%, 25% and 30% extension) is commonly used throughout the industry.

When keratin fibers are stretched, the load-elongation curve shows three distinct regions (Fig. 9.2). The lower curve in Fig. 9.2 represents stretching a hair fiber in water. The curve at the top of the chart represents stretching at 65% RH. In the Hookean region of the load–elongation curves, the stress (load) is approximately proportional to the strain (elongation). The ratio of stress to strain in this region is called the elastic modulus (E_s) or more commonly Young's modulus. Only a few

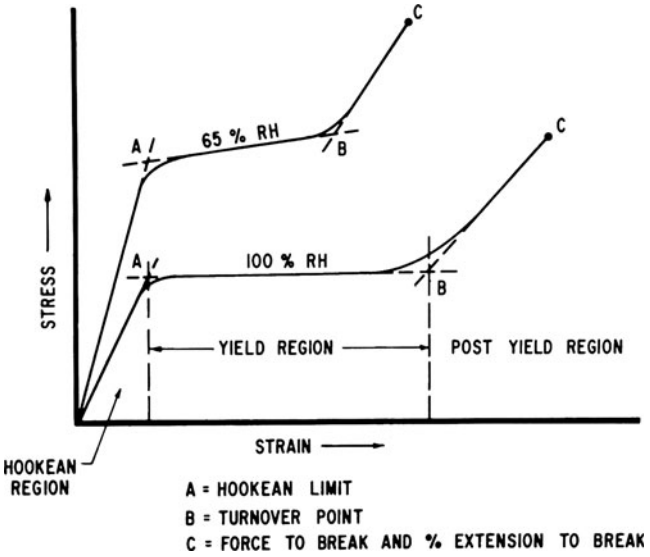

Fig. 9.2 Schematic diagram for load–elongation curves for human hair fibers

years ago, the elastic modulus was normally expressed in units of dynes/cm^2. Today it is usually expressed as GN/m^2 (Giga-Newtons per meter squared or (GPa) although Mega-Newtons per meter squared (MPa) is also acceptable) and may be calculated from this simple expression:

$$E_S = H\ g\ L / A\ \Delta L$$

where H = Hookean slope in g/mm elastic extension, g = gravitation constant (980.6 cm/s^2), L = fiber length in cm, ΔL = fiber extension in cm, and A = fiber cross-sectional area in cm^2. This provides the elastic modulus in dynes/cm^2 which is converted to GN/m^2 by dividing by 10^{10}.

The elastic modulus for stretching human hair, determined in our laboratories at 60% RH and room temperature, is 3.89×10^{10} dynes/cm^2 or 3.89 GPa which is 3,890 MPa. More data on the elastic modulus from other laboratories is described later in this chapter. Methods other than load–elongation have been used to determine the elastic modulus of hair fibers. These methods [10, 11] are also described later in this chapter.

Other important parameters of load–elongation curves are the Hookean limit (Fig. 9.2, Point A), the turnover point (Fig. 9.2, Point B), the percentage extension to break, the stress to break (in the fiber industry called "tensile strength" but more realistically called the extension to break), the post yield modulus (stress/strain) in the post yield region, and the work of elongation (the total area under the load–elongation curve).

An interesting study by Hamburger et al. [12] more than 60 years ago suggested that the pullout energy of cosmetically unaltered Caucasian hair at 65% RH is approximately equal to the Hookean limit which is considerably less than the stress to break. Berthiaume et al. [13] published results more than 40 years later showing that the pullout load for Caucasian hair is about 40–45 g (slightly higher than that of Hamburger et al. [12]), for African hair 30–35 g and for Asian hair 60–65 g. These data suggest that most undamaged hair fibers under stress will pull out before breaking. Scott found that more than one-half of the fibers collected from combing a few heads of female Caucasian hair in our beauty salon contained bulbs and therefore were pulled out; however 5 to about 35% of the hairs were broken. Hair fibers broken on heads actually exhibit different types of fracture patterns. In many cases evidence for cuticle fracturing before catastrophic failure can also be found on hairs growing on live heads, see Chap. 6.

These facts lead one to question the practical implications of tensile testing involving slow extension to break as a criterion for "strength". Impact loading (by Robbins [14]), mechanical fatiguing (by Kamath et al. [15]) and extension cycling (by Gamez-Garcia [16]) seem to more closely simulate the damaging effects of combing and brushing than the slow strain rates and the extreme strains of ordinary tensile testing. See the discussion on these methods and the section entitled, *How Hair Fibers Break During Combing* described in Chap. 10.

Stretching hair fibers under ambient conditions can cause damage, well before catastrophic failure. For example, during stretching or extension at 45% R.H., signs

of cuticle separation and damage occur in regions of the cuticle (cell membrane complex or even the endocuticle) and it occurs sooner in the cuticle of tip ends (about 10% extension) of hair fibers than in the root ends (about 20% extension). Furthermore, this cuticle damage or fracturing [9] occurs sooner than fiber breakage which occurs at about 40–50% extension at moderate humidity and greater than 50% extension in the wet state.

Three important papers on the tensile fracturing of human hair were published by Henderson et al. [17] and by Kamath and Weigmann [18, 19]. These publications show that breaking or fracturing of hair fibers occurs differently in the cuticle versus the cortex and fracturing of hair fibers occurs in different patterns. Figure 9.3 describes the four most common fracture patterns for human hair. The fracture pattern found depends on the extent of hair damage, the relative humidity (whether the hair is wet or dry) and whether or not the fiber is twisted or contains flaws [9, 19].

For wet hair, if the hair and its cuticle are in good condition and near the root end, a smooth break tends to occur, see Fig. 9.4. As the fiber becomes dryer, below 90% RH, step fractures are more commonly observed (Fig. 9.3). Fibrillation and splitting (Fig. 9.3) are distinct cortical fracture patterns and these tend to occur more when the hair is in poor condition especially with oxidative damage and with twisted or kinky fibers [19] and when the relative humidity is low, rather than when the fiber is wet. One reason for that effect is that the cortex is less extensible than the cuticle when the fiber is dry, below 90% RH [17]. See Chap. 6 for electron micrographs illustrating these different fracture patterns for hair fibers.

If the cuticle is in poor condition, split ends can occur upon catastrophic failure. Split ends can also occur from oxidative damage (Chap. 10) and from step fractures and fibrillation, by way of mechanical action and the subsequent abrasive actions of combing and brushing. See the discussion on damage to hair from shampoos, grooming and weathering in Chap. 6.

Stretching in the wet state is very different than stretching in the dry state. This is because failure in the wet state generally involves hydrophilic layers, such as the

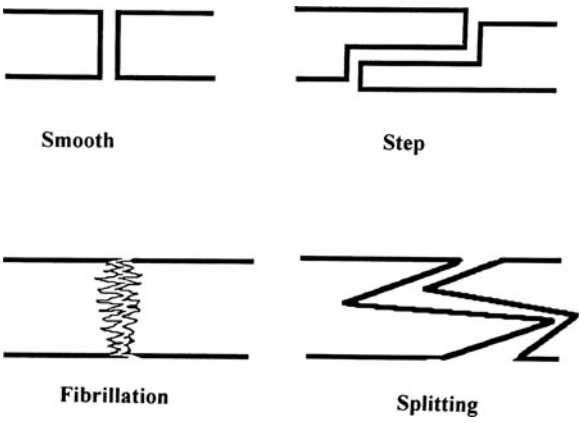

Fig. 9.3 Schematic depicting some of the more important fracture patterns for human hair

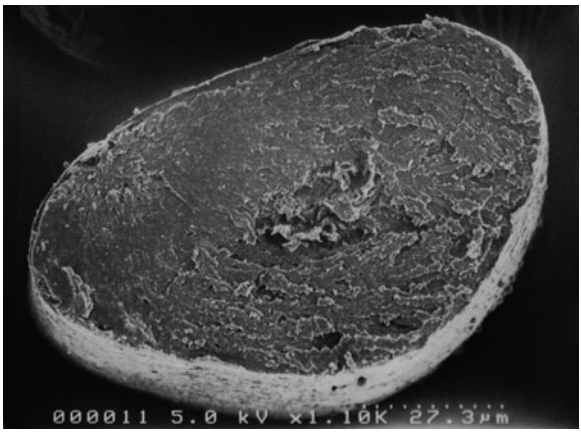

Fig. 9.4 A hair fiber broken by stretching in the wet state illustrating a smooth fracture (SEM kindly provided by Sigrid Ruetsch)

contact zone of the CMC or the endocuticle because it involves breaking bonds in hydrophilic layers. On the other hand, failure in the dry state generally involves breaking bonds in or between hydrophobic layers [20]. For example, failure at the junction of the Beta and Delta layers of the CMC occurs because of the weak hydrophobic bonding between branched hydrocarbons (18-MEA) and relatively short hydrocarbon amino acid side chains of the hydrophobic fibrous proteins in the Delta layer [20]. This site is conducive to failure when the cuticle layers are strained at low moisture levels. Such fractures at 65% RH or lower allow the flow of cuticle past cuticle during fiber extension [21], during extension cycling [20] or even bending.

Beta-Delta failure was originally cited by Negri et al. several years ago [22]. The lower the relative humidity (the moisture content of the hair), the lower the strain required to initiate failure between the upper Beta layer and the Delta layer as noted by Gamez-Garcia [16].

Stretching hair fibers to break in the wet state (approximately 50% extension) often produces what appears to be a clean break that macroscopically resembles a razor cut, see Fig. 9.4. However, on close examination of such breaks, we see that fracturing can occur in the cuticle (see Figs. 9.5 and 9.6) well before catastrophic failure. Extension of hair fibers at low RH and even low percentage extensions generally induces Beta-Delta failure [20–22], as illustrated in Chap. 6. Extension of hair fibers to only 10–20%, at 45% RH (or especially at higher humidities) and very slow strain rates, sometimes induces failure in the endocuticle [23, (Ruetsch, private communication) (see Chap. 6) very likely at or near the junction of the endocuticle and exocuticle. Such fractures result in the separation of the surface scales from the underlying layer producing an uplifting of scales, see Fig. 9.5 and Chap. 6. This type of endocuticular failure is not the norm under normal tensile-loading conditions or faster strain rates that are normally encountered in grooming. More recent evidence indicates that a very slow strain rate at higher humidity causes shear stresses within cuticle scales and leads to this type of failure [23].

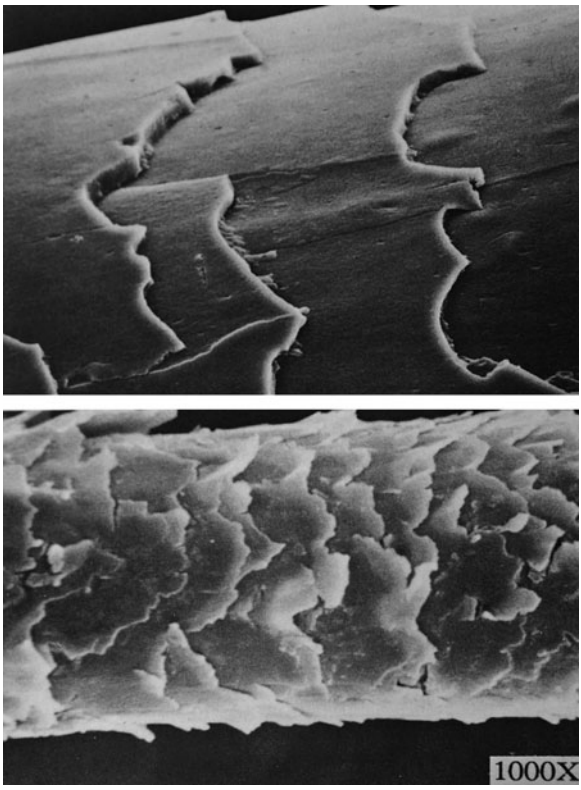

Fig. 9.5 *Top*: Control hair from near the scalp with no lifted cuticle scales. *Bottom*: Hair fiber extended at low RH. Note the scale lifting from extension. Micrographs kindly provided by Sigrid Ruetsch

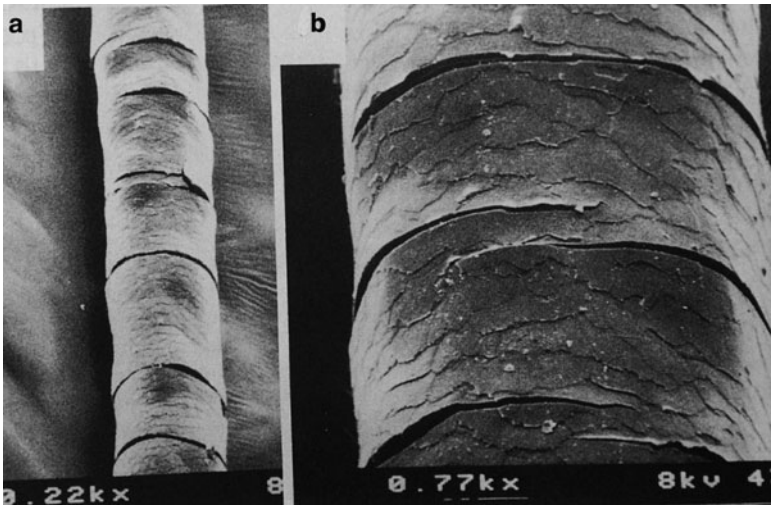

Fig. 9.6 Cracking of the cuticle caused by extension cycling to 200 strain cycles at 30% extension at 100% RH [16]. This cuticle damage is similar to that caused by stretching hair to break in water (reprinted with permission of the Journal of the Society of Cosmetic Chemist)

Extensions to about 30% or slightly higher, in the wet state, can produce multiple circumferential fracturing of the cuticle, with separation of entire cuticle sections from the cortex [18], see Fig. 9.6. Gamez-Garcia [16] demonstrated that this same type of effect can be produced by extension cycling at even lower extensions at high relative humidity or in water.

Stretching to break in the dry state, below 90% RH but not near 0% RH is more prone to induce uneven cortical fracturing. For example, a step fracture or fibrillated end or even split end is likely to result. Stretching or bending hair fibers as occurs during combing or grooming operations is capable of producing stress cracks in the non-keratin regions, the endocuticle and the intercellular regions. Subsequently, scale lifting can occur in the damaged regions of the hair fiber, see Chap. 6.

A hysteresis similar to that in Fig. 9.7 is obtained, when a keratin fiber is stretched up to 30% of its original length in water and then allowed to return to its original length (in water). Such a curve results in spite of potential cuticle damage (especially at high strains). The work of elongation is always greater than the work of recovery; thus, a hysteresis occurs, and the ratio of these two work values is called the resilience ratio (or hysteresis ratio) [24], another useful load-elongation parameter.

As indicated, we normally take fibers 5 cm long and stretch them to 20% of their length at a rate of extension and recovery of 0.25 cm/min. The rate of extension will influence the tensile results [25]. Sikorski and Woods [26] and Simpson [10] suggested an increase of approximately 5% in the elastic modulus for a tenfold

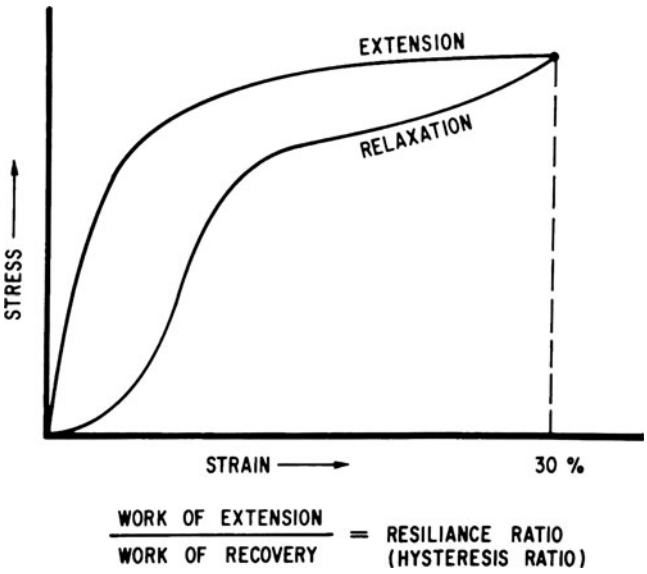

Fig. 9.7 Schematic diagram for load–elongation and recovery curves for human hair fibers

increase in extension rate. Stretching hair fibers to 20% and holding them for 4 h produces a temporary increase in length or a temporary set [27].

After stretching the fibers and relaxing them, as described above, we allow the fibers to relax overnight in water. The fibers can then be treated and re-stretched, thus making before-and-after treatment comparisons on the same fibers. Such a procedure, without treatment, provides reproducible load-elongation curves, confirming the validity of the before and after comparison. Speakman [28] and Sookne and Harris [29] first suggested this type of test procedure. Speakman referred to percentage changes in the work of extension. Harris coined the term "30% index" as the ratio of tensile values to 30% extension. An implicit assumption in this procedure is that calibration or stretching before treatment does not alter the reactivity of the fibers. Wolfram and Lennhoff [30] provided evidence that supports the validity of this assumption, however, at 30% extension cuticular damage occurs that should increase reaction rates for some reactions with stretched hair and may also affect the type of fracture produced. Work and force values to 15% and 25% elongation have also been used [31, 32]. Since calibration elongations, especially in the vicinity of 30% or higher, can produce cuticle damage that is not normally detected in load-elongation parameters stretching hair to lower percentage extensions (15–25%) is preferable.

9.2.2 *The Effects of Relative Humidity on Tensile Extension of Hair*

The moisture content of human hair varies with relative humidity (RH), increasing with increasing RH, (see the section entitled *Influence of Relative Humidity on*

Table 9.1 Elastic modulus (MPa) verses relative humidity of hair and wool fiber

	65% RH		100% RH[a]		Ratio
	Human Hair	Merino Wool	Human Hair	Merino Wool	E_S 65%RH/ E_S 100% RH
Elastic modulus [27]	5,394	3,040	2,059	1,177	Hair 2.62 Wool 2.58
	% RH		Wool E_S at given RH@/ E_S at 100% RH		
	0[b]		2.76		
	32		2.44		
	44		2.27		
	65		2.10		
	78		1.85		
	91		1.41		
	100		1.00		

@ [32]
[a]In pH 7 buffer
[b]In dry glycerine, this approximates 0% RH

Dimensions of Hair in this chapter). Thus changes in the moisture content of hair have a large effect on the tensile properties as shown by elastic modulus changes versus %RH in Table 9.1.

Speakman [33] and Menkart [34] conducted relatively extensive load–elongation studies at several relative humidities for wool fiber. These data show a regular increase in extensibility (percent extension to break) with increasing RH. Even though such extensive studies could not be found in the literature for human hair, undoubtedly a similar relationship exists, because:

1. Tensile properties of hair fibers at 55–65% RH compared with 100% RH (in water) show greater extensibility at the higher humidity (Fig. 9.2) and a lower elastic modulus (Table 9.1) and lower work and force values in general [34].
2. The dynamic elastic modulus of human hair has been reported to respond similarly to changes in RH [35].
3. There is virtually an identical quantitative binding of water to wool and hair as a function of RH [36, 37]. Therefore we conclude a similar stress/strain RH relationship (see Table 9.1).

9.2.3 *Tensile Properties and Fiber Diameter*

Both wet and dry tensile properties of chemically unaltered keratin fibers are directly proportional to fiber diameter. Figure 9.8 summarizes this relationship for the dry tensile properties via a plot of the Hookean slope versus fiber linear density at 62% RH. Since linear density is proportional to cross-sectional area and diameter, the tensile properties are also proportional to fiber diameter. Robbins and Scott [38] reported a procedure for determining both wet and dry tensile properties on

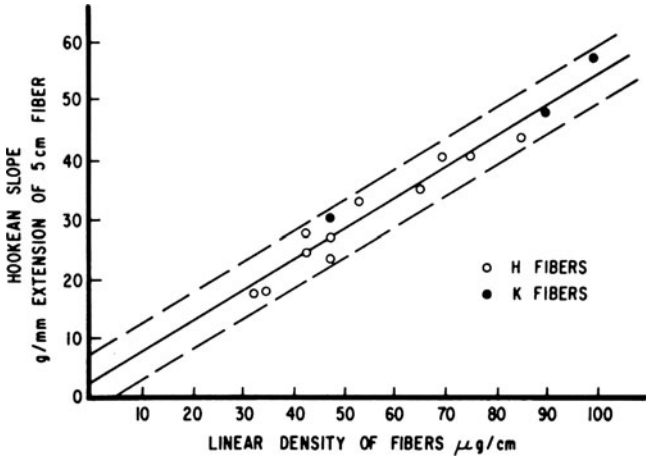

Fig. 9.8 Hair fiber elastic extension versus linear density (Reprinted with permission of the Journal of Cosmetic Science)

the same fibers from only one of these properties. This procedure depends on this fundamental relationship, that is wet and dry tensile properties are proportional to fiber diameter, and therefore, proportional to each other. An equation for predicting the dry Hookean limit at 60% RH from the Hookean limit in water (X) is: Y ± 3.75 = 2.18 X and for predicting the dry stress to break (B) at 60% RH from the wet force to 20% extension (F) is: B ± 10.3 = 3.92 F.

9.2.4 *Tensile Properties and Temperature*

Rebenfeld [39] compared human hair with wool fiber by studying the effect of temperature on the load–elongation properties in neutral buffer solution,. Increasing temperature has an effect similar to increasing humidity on the shape of the load–extension curve [39, 40] (see Table 9.2). The elastic modulus for both human hair and wool fiber decrease with increasing temperature, but are lower for wool at any temperature, probably because of its lower cross-link density. The post-yield modulus and tensile stress at break decrease with increasing temperature, whereas extensibility increases.

The breaking stress = M g/A where M = load in kg, g = standard gravity = 9.81 N/kg and A is the cross sectional area in meters squared.

$$\text{Elastic modulus} = \frac{\text{Mg} / \text{A}}{\Delta\text{L}/\text{L}}$$

where M = kg; g = standard gravity 9.81 N/kg; A is the cross sectional area in meters squared and ΔL/L is 2.0 and constant from 65% to 100% RH while it varies from 4.08 at 0% RH, to 3.21 at 17.7% RH and 2.58 at 44.2% RH as shown by Feughelman and Robinson [32].

The turnover point (extension to B in Fig. 9.2) undergoes a transition at 85.5°C for unaltered hair and at 66°C for partially reduced hair. Rebenfeld explained these

Table 9.2 The influence of temperature on the stress/strain properties of human hair[a]

	pH 7		
Temperature C°	Elastic modulus MPa	Stress at break[b] MPa	% extension At break
21	2,080	168	48
35	1,770	129	
50	1,670	125	50
70	1,640	140	
90	1,360	99	72

[a]Calculated from data by Rebenfeld et al. [39]

[b]By convention, the H term is in force/mm elongation for the elastic modulus, while it is in force units for the stress to break fibers and one divides by the quantity ΔL/L for the Elastic Modulus, see the equations above

results in terms of a disulfide–sulfhydryl interchange mechanism, whereby stressed disulfide bonds are relieved and transformed into stress-free positions at higher temperatures.

Crawford (private communication) examined the effect of temperature in a dry atmosphere on the wet tensile properties of hair. Crawford found significant changes in the force to 20% extension after heating to 100°C, 25 times for 15 min intervals. Permanent-waved hair appeared to be more susceptible to heat, undergoing a decrease of approximately 7%, as compared to 4% for unaltered hair. McMillen and Jachowicz [41] examined the effects of hot iron treatments on hair and identified a decrease in tryptophan level due to thermal induced decomposition, a small increase in the combing force and a yellowing effect on white hair. However, these scientists did not report tensile effects. A thermo-chemical technique for analysis of human hair has also been reported by Humphries et al. [42]. For discussion of stress strain models see the section entitled *Stretching Hair and Stress Strain Models* in Chap. 1.

9.2.5 Twisting and Stretching Normal Hair and Hair with Natural Twists

Dankovich et al. [43] examined the effects of twisting hair fibers before and during stretching to determine the effects of twisting on tensile properties. They used two experimental procedures: One in which the hair was twisted at constant length, followed by extension to break while not allowing untwisting and the second procedure involved twisting and then untwisting at constant length followed by extension to break. Twisting an 80 micron hair fiber 45 turns/cm produced catastrophic failure. Therefore lower levels of twist were examined: 11, 23 and 38 turns/cm. Only small changes were produced in the stress and strain to break using 11 turns/cm. However, large changes were produced in the Hookean (decrease in Modulus) and yield regions (increase in Modulus). Extensive changes were produced in all stress strain parameters while simultaneously twisting at higher levels (23 and 38 turns/cm). These scientists concluded that the combination of tensile and torsion stresses (at these twist levels) weakens human hair fibers, but these levels of twist are far beyond what is normally encountered in actual practice on live heads.

The degree of recovery from twist deformation was examined after the fibers were relaxed for 5–10 min before stretching. Dankovich et al. [43] concluded that the tensile properties of human hair are recoverable from twist deformations at low and moderate twist levels as normally encountered in routine grooming operations. When the fibers were twisted and then allowed to untwist the tensile stress and strain did not change relative to controls, however, the initial modulus decreased with increasing levels of twist [43].

By examining scanning electron micrographs Dankovich et al. [43] found that twisting and untwisting hairs can produce cuticular damage which doesn't show up

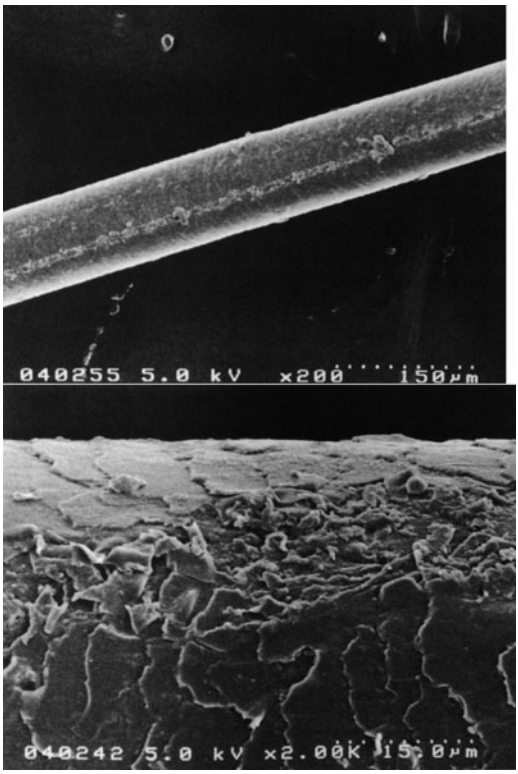

Fig. 9.9 Results of twisting a highly elliptical hair fiber [43]. *Top*: Note damaged "line" where cuticle scales converge upon twisting. *Bottom*: Note the damage effect at higher magnification (reprinted with permission of the Journal of Cosmetic Science)

in tensile testing. This result supports the conclusion of Robbins and Crawford [7] that tensile properties are a property of the cortex with negligible contribution from the cuticle. When a highly elliptical hair is twisted (even at low twist) the cuticle cells are compressed into one another creating damage to the scales, see Fig. 9.9. This scale damage does not occur to the same degree in more circular hair fibers (because of less scale overlap). The effect of twisting hairs and hair damage is described in more detail later in this chapter. The above experiments involved the effects of twisting hairs on the tensile properties, and not effects of natural twists on the extension behavior as examined by Kamath et al. [19] and described later in this chapter.

9.2.6 Tensile Properties of Different Geo-Racial Groups

Data from six different laboratories was compiled comparing the breaking stress for both Caucasian and African type hair at 65% RH and room temperature [19, 44, 45]. The average breaking stress for Caucasian hair was 187 MPa. The average for

African hair was 151 MPa. These data as analyzed by the matched pairs *t*-test were significantly different showing that African type hair requires a lower stress to break than Caucasian hair. Unfortunately insufficient experimental details were described in some of these studies to determine the length of the fibers tested, the position on the scalp and age/weathering, and whether or not data for some hairs were rejected for breaking before entering the post yield region.

Relevant to these points is the fact that Duvel et al. [46] on Caucasian hair showed about an 8% loss in the tip ends of 41 cm hair fibers for the tensile breaking stress. This tensile loss could not be detected at 16 cm from the scalp end, but was detected between 16 and 24 cm from the scalp end (about 1 and 1/2 year's growth). These scientists also found a gradual loss of both covalently bound lipid and free lipid from the hair. Duvel et al. proposed that this ongoing loss of both free and covalently bound lipid by weathering actions leads to an increased susceptibility of the proteins of the cortex to degradation and eventually to a loss in the tensile breaking stress. Regrettably, data of this sort was not found for curly African type hair where weathering including grooming actions leads to small cracks in the hair [19] and appears to be more severe. However, long African hair is difficult to obtain for such a comparison because of its fragility.

Kamath et al. [19] demonstrated on African American hair (chemically untreated and not treated with hot irons) from one male that the breaking stress was very low at 123 MPa (ellipticity 1.89; indicative of a very high curvature probably Type VIII [47]). These scientists compared this hair to their earlier work on Caucasian hair [18] (also at 65% RH and room temperature) where the breaking stress was found to be approximately 200 MPa (pooled European dark brown hair, average ellipticity 1.17) to 220 MPa (highly elliptical, index = 1.6 Caucasian hair from one individual). Kamath, Hornby and Weigmann demonstrated that the African type hair had twists and at 65% RH, 22% of the fibers broke before 20% extension. When this "premature failure" occurred, Kamath, Hornby and Weigmann observed that the fibers often broke in a region of fiber twist. This effect was confirmed by examination of the broken ends of the hairs, see Fig. 9.10. Furthermore, Kamath, Hornby and Weigmann found that the cross-sectional area varied widely in the region of twist, see Fig. 9.11.

Kamath, Hornby and Weigmann found "premature failure" to be more prevalent in the dry state than the wet state (in fact it was virtually non-existent in the wet state) and concluded that premature failure was due to natural structural flaws in the twists of the fibers or flaws produced by mechanical damage associated with grooming actions. Of the seven hair types that Hardy [48] examined, he noted the highest frequency of kinks or twists in the most highly coiled hair with the most from African type hair.

Pili torti (Fig. 9.12, also see Chap. 3) is a congenital deformity resulting in highly twisted hair fibers and can be confused with highly twisted African hair, but it is even more twisted than kinky hair of Africans. In this disease, hair fibers often break in a twisted region only a short distance from the scalp because of defects created by natural twists in the fibers. The susceptibility of highly twisted Pili torti hair fibers to breakage supports the work and conclusions of Kamath et al. [19]

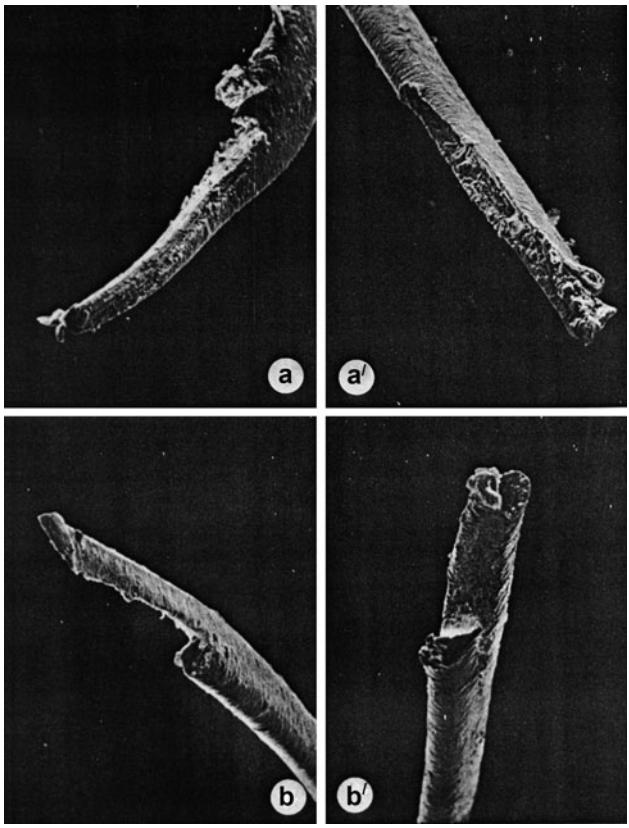

Fig. 9.10 An African American hair fiber broken in the region of twist [19] (reprinted with permission of the Journal of Cosmetic Science)

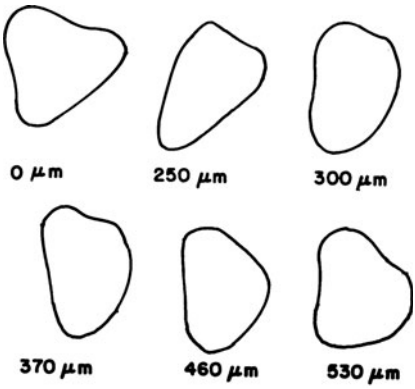

Fig. 9.11 Outlines of varying cross-sectional shapes of an African American hair fiber in the region of twist from Kamath et al. [19]. Note the large deviations from circularity (reprinted with permission of the Journal of Cosmetic Science)

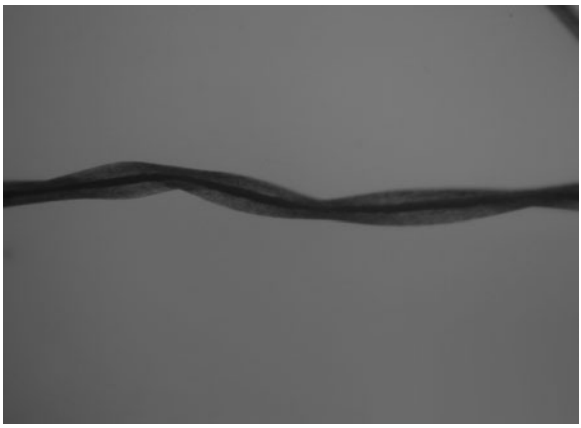

Fig. 9.12 Pili Torti or twisted hair, an example of a congenital deformity in which an extremely twisted hair is produced and it tends to break easily in the regions of twists (also see Fig. 3.3). Light micrograph, kindly provided by John T. Wilson

showing that premature fractures and breakage of hair fibers of African type hair occur in the region of natural twists.

Porter et al. [47] found that the tensile properties of African hair (curl Type IV to VIII) for more than 12,000 hair fibers (65% RH) tends to decrease with increasing fiber curvature, $R^2 = 0.66$. Therefore, for African type hair 66% of the variation in breaking stress, a decrease from 206 to 173 MPa from curl Type IV to curl Type VIII can be accounted for by hair fiber curvature or effects associated with curvature such as twists or kinks, fiber composition and/or mechanical damage from grooming conditions. Porter et al. indicated that in their work, tensile properties were measured on the first 50 hairs that showed "normal failure profiles". This suggests that data from those hair fibers that displayed "premature failure" were rejected providing higher values for the breaking stress in Porter's work than in some of the other studies such as the study by Kamath et al. [19] or even for some comparisons with data for Caucasian or Asian hair.

The breaking stress for chemically untreated Caucasian hair fibers at 65% RH from 11 different laboratories/scientists [10, 18, 43–45, 49–51] averages 197 ± 15.8 MPa with an upper 95% mean of 207.6 and a lower 95% mean of 186.4 MPa. A similar distribution analysis of African hair for breaking stress from seven different laboratories [19, 44, 45, 47] over the curl range of IV to VIII shows a mean of 156.6 ± 31.7 with an upper 95% mean of 185.9 and a lower 95% mean of 127.4 MPa suggesting a lower mean and more variation for the African hair data.

Unfortunately we do not know with certainty the curl type range covered by the Caucasian hair in these studies, but it likely covers curl Types I to III and possibly I to IV. Therefore, these data suggest a larger effect of curvature on breaking stress over the curvature range of curl Type VI to VIII for African type hair than for Caucasian hair over the curvature range of curl Type I to III or IV which is most likely from weakening of the fibers from higher grooming forces for the higher curvature hair. In addition a correspondingly higher ellipticity range [47] should result in more and larger twists which would produce more natural flaws and weaker fibers.

The breaking stress from three different laboratories which directly compared Asian versus Caucasian hair averaged 191.1 MPa for Asian and 191.8 for Caucasian hair at 65% RH and room temperature, thus no significant difference. One of these studies compared 50 hairs from each geo-racial group (TRI-Princeton was the testing lab) while the number of hairs in the other two studies were not specified [45]. These data suggested no significant difference in the breaking stress of Asian versus Caucasian hair; however because of the larger diameter and lower ellipticity of Asian hair I would recommend additional study with many more hairs over all relevant curvatures for these two hair types before this conclusion is accepted.

Porter et al. [47] showed that for 12,050 African type hair fibers, Young's modulus decreases with increasing fiber curvature from 3,147 MPa for curl class IV to 2,670 MPa for curl class VIII. Young's modulus for Caucasian hair from seven different laboratories [10, 18, 43, 49–51] was compiled and a distribution analysis showed an average of 3,478 MPa with an upper 95% mean of 3,859 and a lower 95% mean of 3,098 MPa. Therefore, Young's modulus for stretching Caucasian hair (about 1–2% stretch) tends to be higher than for "average" African type hair. Whether or not Young's modulus for African hair of curl class IV is equivalent to that of Caucasian hair or other curl class IV hair will require direct testing.

Scott and Robbins [49] found no significant difference between Young's modulus for stretching Korean hair versus Caucasian hair, but this was on a limited number of fibers (25 from each group). In theory if the internal structures of Asian and Caucasian hairs are sufficiently similar we would expect the same Young's modulus for these two hair types.

9.2.7 Chemical Bleaching of Hair and Tensile Properties

Chapter 5 describes the chemistry of bleaching human hair. A major side reaction in the bleaching of hair involves the oxidation of cystine cross-links to cysteic acid residues. This disruption of disulfide cross-links in the cortex has a major influence on the wet tensile properties of hair. Alexander et al. [52] oxidized wool fibers to different extents with peracetic acid and determined the work required to stretch the fibers, both wet and dry, and the cystine contents of the fibers. They concluded that the disulfide bonds contribute largely to the wet breaking stress of the fibers. Furthermore, the wet breaking stress decreased almost linearly with the cystine content. In contrast, the dry breaking stress was virtually unaffected by disulfide bond rupture. In fact, Alexander et al. [53] found a weakening in the dry state only after more than 60% of the cystine cross-links were broken.

Harris and Brown [54] reduced wool fibers to different extents and methylated the newly formed thiol groups to prevent recombination to disulfide bonds. These scientists then determined changes in the 30% index of these fibers. Their conclusions were much the same as those of Alexander et al. [53], that is the wet breaking stress decreased with the cystine content but the dry breaking stress was virtually unaffected by cystine content except at high percentage rupture. Garson

Table 9.3 Tensile properties of frosted hair[a]

Tensile parameter	Nonfrosted hair	Frosted hair	% loss in tensile property	% loss in cystine
Wet tensile properties				
Work to extend 20%	13.34	5.50	59	48
Hookean slope	13.25	5.79	56	48
Hookean limit	13.30	5.19	61	48
Force to extend 20%	16.67	7.01	58	48
Resilience ratio	0.587	0.585	0	48
Dry (55% RH) tensile properties				
Work to extend 20%	32.06	30.84	4	48
Force to extend 20%	36.71	33.80	8	48
Resilience ratio	0.173	0.115	44	48

Note: Work to 20% extension is g × cm, Hookean slope is in g force/mm elastic extension, Hookean limit is g, and force to 20% extension is g

[a]Data are normalized to a 70-μm diameter basis at a length of 5 cm

et al. [55] measured the dynamic elastic properties of hair fibers. They found similar effects. These scientists found that the effects of oxidation are greater when measurements are made in water than at relative humidity ranging from 0% to 80%.

Oxidative bleaching of human hair on live heads provides similar results for the tensile properties. Robbins and Kelly [56] examined both the wet and dry tensile properties of frosted and non-frosted hair fibers from the same person (Table 9.3) that is hair that had been frosted on the head. Except for the resilience ratio, the loss in dry tensile properties was less than 10%, but the loss in wet tensile properties approached 60% at 48% disulfide cleavage. Therefore, these results are similar to the oxidation of wool fiber by Alexander et al. [53].

Alexander et al. [53] also suggested that both the dry and wet breaking stress of wool fibers are greatly influenced by peptide bond cleavage, but cleavage of the disulfide bond primarily affects the wet breaking stress. This effect likely occurs by breaking of crosslinks in the fiber and an increase in the water binding capacity of the fibers in critical regions of the cortex. The frosting treatment is an alkaline peroxide-persulfate system capable of some peptide bond cleavage, which likely accounts for the small losses in dry breaking stress. Peptide bond cleavage also likely accounts for the difference between the percentage decrease in cystine and the percentage loss in wet tensile properties.

Interestingly, the percentage change in the dry resilience ratio, an estimate of the ability of the fibers to recover from extension into the yield region, approximates the loss of cystine cross-links. Additional work is necessary to determine the significance of this observation. The above discussion suggests that the percentage loss in cystine, as estimated by cystine or cysteic acid analysis, is a good estimate of the loss in tensile properties of hair bleached by current "in use" treatments.

Since frosting of hair is an extreme bleaching treatment, an obvious question is to what extent milder bleaching treatments affect the tensile properties of hair. Several papers [56–58] describe bleach damage to hair either by cystine or cysteic

acid analyses [57] or by tensile properties [31, 58, 59]. In summary, these papers suggest that "in use" bleaching of hair commonly produces decreases in the wet tensile properties of up to 25%, with greater losses occurring when the fibers are frosted or stripped and in many cases of "in use" bleaching the changes in the dry tensile properties are very small and close to the limits of detection.

9.2.8 Permanent Waving Hair and Tensile Properties

Chapter 4 describes the chemistry of the reactions of permanent waves with human hair. Permanent waving involves reduction of disulfide cross-links accompanied by molecular shifting of proteins by bending the hair on rollers followed by mild re-oxidation. These reactions produce large changes to the tensile properties of the fibers during reduction but smaller changes after re-oxidation.

Data by Crawford (private communication) (see Table 9.4), using hair waved in the laboratory with a commercial home permanent at a 4:1 solution-to-hair ratio and then re-oxidized, showed a decrease in the tensile properties of approximately 5–20%. Beyak et al. [31] confirmed this finding for the wet tensile properties of permanent waved hair. This amount of tensile damage appears to be typical for a "normal" permanent-wave treatment, where approximately 20% of the disulfide bonds are ruptured during the reduction step [56]. Other reports in the literature, for example the paper by Tate et al. [60] show larger decreases in the wet tensile properties from permanent waving. Such effects are most likely from laboratory permanent waving as opposed to on head treatment and lab tests often involve a larger than "in use" solution to hair ratio.

Higher concentrations of mercaptan, higher pH [61], and higher solution-to-hair ratios all produce more extensive reduction [59, 62] and ultimately more tensile damage. The decrease in dry tensile properties is less than in the wet state. This is in agreement with the work of Harris and Brown [54], who showed that up to 60% elimination of disulfide bonds in keratin fibers, by reduction and methylation, produces only small effects on the dry tensile properties (65% RH). However, the wet tensile properties decrease almost linearly with the disulfide content.

Garson et al. [55] measured the dynamic elastic properties of hair and demonstrated that permanent-waving, similar to bleaching, provides greater changes to the elastic properties of hair in water than at relative humidity from 0% to 80%.

Table 9.4 Effect of permanent waving on the tensile properties of human hair (Crawford, private communication)

	Stress to break		Stress to extend 20%	
	Dry (65% RH)	Wet	Dry (65% RH)	Wet
Commercial home Permanent wave	−7%	−15%	−11%	−18%

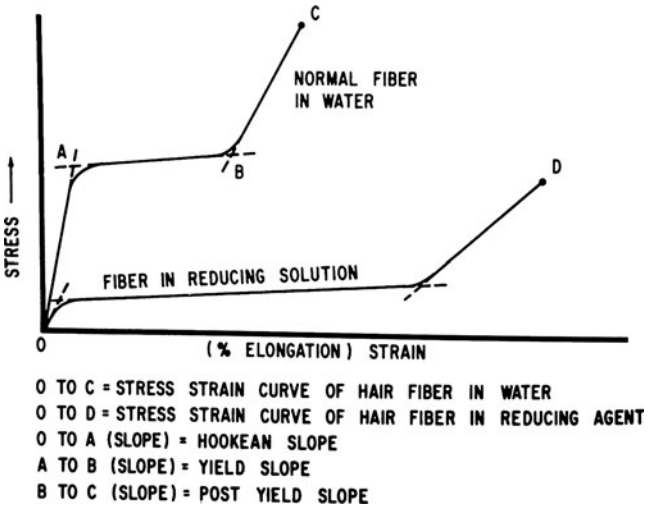

Fig. 9.13 Schematic diagram representing stress/strain curves for a hair fiber in reducing solution compared to a hair in water

Presumably, certain hydrogen bonds are inaccessible to water in "virgin" hair. However, elimination of specific disulfide bonds by oxidation and/or permanent-waving renders these additional hydrogen bonds accessible to liquid water or even at high regains (over 80% RH). Therefore, under these conditions those bonds are broken by water thus lowering the wet tensile properties more than the dry tensile properties.

Stretching hair fibers in aqueous solutions of reducing agents, compared to water, results in lower required stresses to achieve a given strain (see Fig. 9.13). This effect is due to the rupture of disulfide bonds, the breaking of hydrogen bonds, and molecular reorientation. Treatment of reduced hair with mild oxidizing agents (neutralization) increases the tensile properties, approaching the properties of the original untreated fibers. Such occurs if the fibers have not been reduced too drastically (beyond 30–50% disulfide rupture).

Load-elongation [63] and stress-relaxation [64] measurements may be used to follow the course of the reduction of keratin fibers by mercaptans. Extension into the post yield region is resisted primarily by the disulfide bonds [63], which is one reason that this region of the stress/strain curve holds special significance to the reduction reaction. However, Wortmann and Souren [65] pointed out that the main effect of reduction or the cleavage of disulfide bonds may be on the crystalline filaments. More specifically, the effect is likely on the interactions between the crystalline and surrounding structures rather than on the disulfide bonds themselves. Thus, the wet tensile properties serve as a valuable tool for studying the reduction of hair [61–66] its re-oxidation [63, 67], and the effects of the total cold-wave process [31, 58].

9.2.9 Alkaline Straightening and Tensile Properties

Alkaline straightening degrades both cystine and peptide bonds. Therefore, alkaline straightening must decrease both the wet and dry tensile properties of human hair. Nevertheless, I have not been able to find data in the literature to support this rather obvious conclusion. Data from Kamath et al. [15] demonstrated by fatiguing experiments that hair is weakened by alkaline straightening treatments. The hair used in this study was from a Black male age 31. This hair had never been treated with chemical or heat treatments. Both an alkaline and reduction type relaxer was shown to weaken the hair. With the alkaline straightener 8% of the fibers broke during treatment. In comparison, for the thioglycolate reduction treatment zero fibers broke during treatment. This effect shows more damage by the alkaline straightener in spite of the fact that a chemical neutralizer was not used after the reduction treatment by the thioglycolate system.

The fatiguing process involves attaching weights to the fibers and then dropping the weights repeatedly to stress the hair similar to the way it might be fatigued by continuous combing of the fibers. The data shows the largest distinction between untreated and treated fibers using the smaller rather than the larger weights. Therefore, the data (with smaller weights) are probably the most meaningful indicator of damage to the hair. These data clearly show that the hair is weakened or damaged by both treatments; however, more damage is indicated by the alkaline straightener than by the thiol type relaxer [15].

9.2.10 Dyes and Surfactants and Tensile Properties

Chapter 7 describes the chemistry of oxidation and ionic dyes in detail. Oxidation dyes are by far the most prevalent hair dyes, and consist of aromatic amines and phenols [68–70] that condense with each other and possibly with electron-rich side chain groups in hair. Oxidative dyeing is done in the presence of an oxidizing agent such as hydrogen peroxide at a pH of up to 10. The concentration of peroxide and alkali required depends on the difference between the starting hair color and the desired shade. Therefore, the primary tensile damage to hair by oxidation dyes depends on the extent of accompanying disulfide oxidation (bleaching) that occurs in the cortex of the hair. In theory, dyeing hair from a darker to a lighter shade should produce more wet tensile damage than dying hair from a lighter to a darker shade; however the more important factor is the extent of oxidation that occurs to the hair proteins in the cortex regardless of the shade difference.

Crawford (private communication) found small losses in tensile properties in hair dyed from a lighter to a darker shade with a commercial oxidation dye. Pande et al. [71] found 5–8% loss in the wet tensile properties (to 15% extension) for Permanent hair dyes and 2–6% loss for Demipermanent dyes. Pande et al. also

found that hair dyes provide protection from oxidative sun damage. In addition, the darker the dyes the more sun protection provided.

The tensile damage to hair by anionic and cationic surfactants or dyes in single treatments that is by short time intervals (hours) and moderate pH's is negligible. Zahn [72] examined the effect of anionic and cationic surfactants on the 25% index of wool and hair. Soaking wool fibers in sodium dodecyl sulfate for 7–41 days produced a decrease of only 6% in the 25% index. Shorter time intervals produced even less wet tensile damage. Zahn [72] indicated that for human hair the decrease is approximately one-half that of wool fiber, and these effects are reversible with water. Zahn indicated slightly larger effects from cationic surfactants. Scott (private communication) examined the stress/strain properties of hair after treatment with a cationic surfactant and found negligible changes. These results test the effects of surfactants on "chemically unaltered" hair, in single treatments, with no mechanical stresses applied. Interactions with other treatments were not considered.

Robbins and Reich, in unpublished work, conducted experiments showing that surfactants and mechanical stresses in combination (short-term treatments (min) attempting to simulate "in use" conditions) can damage the cuticle. But, damage to only the cuticle will not be demonstrable through changes in the tensile properties, a primary weakness of this type of test procedure.

Duvel et al. [46] cut long Caucasian hair into five sections from root to tip end and extracted and analyzed these sections by thin layer chromatography. These scientists showed three classes of major polar lipids including ceramides, glucosyl-ceramides and cholesterol sulfate. In addition, they found as expected that the concentrations of all of these lipids as well as covalently bonded fatty acids decreased with increasing distance from the root end. The data on tensile properties also decreased as one moved from root to tip end. These scientists concluded that the progressive loss of structural hair lipids is a result of normal weathering of hair and grooming actions. Thus, weathering and grooming may help in some manner to contribute to the decrease in the tensile properties of the hair rather than to attribute the decrease in tensile properties to the loss of hair lipids alone.

9.2.11 pH and Tensile Properties

Speakman and Scott [73] found that the influence of pH on the tensile properties of human hair parallel the effects of swelling and pH on wool fiber. Valko and Barnett [74] showed that hair displays a minimum in swelling from pH 2 to 9 with a slight increase in swelling below pH 2 and a larger increase in swelling above pH 9, using extended soaking times (Fig. 9.14).

Breuer and Prichard [75] determined that when human hair is exposed overnight to solutions with pH values <2, it undergoes irreversible structural changes producing a decrease of up to 30% in the 20% index. Hydrolysis and structural rearrangements most likely occur from such a harsh acid treatment.

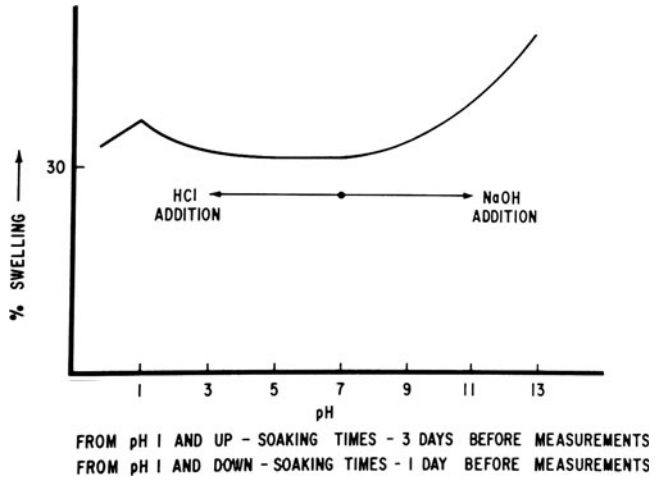

Fig. 9.14 Swelling of hair and changes with pH

9.2.12 Light Radiation and Tensile Properties

Sunlight and ultraviolet light have been shown to decrease the 15% index (in distilled water). Beyak [76] related this effect to the total radiation on the hair. These findings were interpreted as photochemical degradation of disulfide bonds and have been confirmed by Robbins and Kelly [77]. These scientists analyzed amino acids of both proximal and distal ends of human hair and found a significantly larger amount of cysteic acid and a significantly smaller amount of cystine in distal ends. Harris and Smith [78] provided evidence for ultraviolet disruption of cystine in wool fiber. Dubief [79] used the 15% index to follow changes induced in hair using different radiation sources and found about a 40% decrease in the 15% index after 3 months of summer sun exposure on a Paris rooftop. This effect calculates to about a 3 month Florida sun exposure of UV radiation for 24 h per day. See Chap. 5 for a discussion of the chemistry of these reactions and Chap. 10 on hair breakage.

Changes in the cuticle–cuticle CMC such as oxidation of the tertiary hydrogen atoms of 18-MEA has also been reported by Korner et al. [80] however such changes to the cuticle-cuticle CMC will not show up in tensile testing.

9.2.13 Hair Abnormalities and Tensile Properties

Korastoff [81] examined human hair from patients with hypothyroidism and acromegaly and showed a characteristic alteration in the yield region of the stress/strain curve (at low humidity) compared to hair from control groups. Swanbeck [82]

determined that patients suffering from congenital ectodermal dysplasia have hair of low tensile breaking force.

Monilethrix is a genetic anomaly in which hair fibers contain periodic constrictions along the fiber axis (see Chap. 3). Wilson [83] demonstrated that monilethrix hairs tend to fracture at these constrictions and therefore I conclude must exhibit abnormal stretching behavior. Trichorrhexis nodosa is another abnormal condition, wherein hair fibers contain nodes at irregular intervals along the fiber axis (see Chap. 3). These nodes actually contain tiny fractures and the fibers tend to form broom-like breaks [83] under stress. Therefore, nodosa hair fibers should also exhibit abnormal stretching behavior with premature failure at low strain levels. Pili torti is another congenital deformity in which severe twists occur in the fibers resulting in hair fibers that break easily. Therefore Pili torti hair must exhibit weak tensile behavior. Other hair shaft anomalies such as trichothiodystrophy and Menkes syndrome should also display abnormal stretching behavior consistent with the abnormal hair shaft condition associated with these diseases, see Chap. 3.

9.2.14 Reductive Polymerization in Hair and Metal Salts and Tensile Properties

Anzuino and Robbins [84] carried out in situ polymerizations of vinyl monomers in human hair. These scientists then studied the reactions of the polymer-containing hair with metal salts via wet load-extension testing. This reductive polymerization reaction decreased the wet tensile properties by approximately 15%. These scientists found that mercuric acetate treatment of hair containing polydimethylaminoethyl methacrylate, polyacrylonitrile, and polyethylene glycol monomethacrylate were the most effective systems for increasing wet load–extension properties. Although cross-linking through metallic bonding was proposed, an alternative mechanism involves reducing the water binding capacity of the fibers by the polymer and metal taking up space that could be occupied by water in critical water binding regions of the cortex.

9.3 Other Approaches to Evaluate Stretching Properties of Hair

Several other approaches have been used for studying the stretching properties of human hair. Among these approaches are vibration methods [10, 11], stress relaxation [64], stretch rotation [85], set and supercontraction [27], fatiguing [15] and extension cycling [16]. Several of these approaches will be described in some of the next sections of this chapter.

9.3.1 Vibration Methods

In this scheme, a fiber is attached to a beam with a known natural resonant frequency. Tension (within the Hookean region) is applied to the fiber. The beam is then deflected, and, from the change in the oscillation frequency of the beam with the fiber attached, and the natural resonant frequency of the freely vibrating beam, one can calculate the elastic modulus of the fiber. Huck and Baddiel [11] and Garson et al. [55] used this type of system to evaluate the elastic properties of human hair fibers. Huck and Baddiel attached both ends of hair fibers to an oscillating beam. This set up contained a third point of attachment in the middle of the fiber for applying tension. From the following expression, they calculated the elastic modulus:

$$E_S = \frac{8\prod^2 IL\left(B^2 - B_o^2\right)}{A\,Z\,L^2}$$

B = the oscillation frequency with the fiber in position, B_o = the natural resonant frequency of the beam, L = the fiber length, I = the moment of inertia of the beam, A = the fiber cross-sectional area, and Z = the distance between the fiber ends.

The elastic modulus by this "dynamic" method is slightly higher than by load extension, a "quasi-static" method. Tests involving elastic deformations, where either stress or strain is held constant, are called static tests. In quasi-static tests, stress or strain is changed slowly with time, and in dynamic tests, stress and/or strain are varied rapidly with time.

9.3.2 Stress Relaxation

Stress relaxation is a technique in which the fiber is stretched to a given length, treated, and maintained at the stretched length while the decaying stresses are followed with time. Kubu and Montgomery [64] used this technique to follow the kinetics of the reduction of wool fiber. Robinson and Rigby [86] examined both wool and human hair fiber by stress relaxation. These scientists found differences along the axis of the fibers which they attributed to a decreasing free mercaptan level further from the root. This effect provides for less disulfide-mercaptan interchange and a slower rate of stress relaxation as the distance increases from the scalp.

9.3.3 Stretch Rotation

Hirsch [85] studied the elongation of hair under a steadily increasing load, together with a rotational movement. He attempted to explain this combination of stretching and torsion in terms of molecular structure. See the section on the torsional properties of hair in this chapter.

9.3.4 *Set and Supercontraction*

Brown et al. [87] defined set as a treatment that enables a keratin fiber to maintain a length greater than its original length. Chapter 4 describes setting as it relates to the cold-waving or permanent wave process. Supercontraction is not a stretching phenomenon. It is the condition in which a keratin fiber is fixed (by treatment) or held at a length less than its original length. Supercontraction is related mechanistically to setting and is also described in Chap. 4.

9.4 Bending and Fiber Stiffness

When a fiber is bent (see Fig. 9.15), the outer layers of the arc of the bent hair (A) are stretched, and the inner layers (C) are compressed. A region in the center, the neutral plane (B), is unchanged in length. Stiffness is simply the resistance to bending and is an important fundamental fiber property [88]. Recent evidence shows that bending stiffness of single hairs is very important to hair handle or

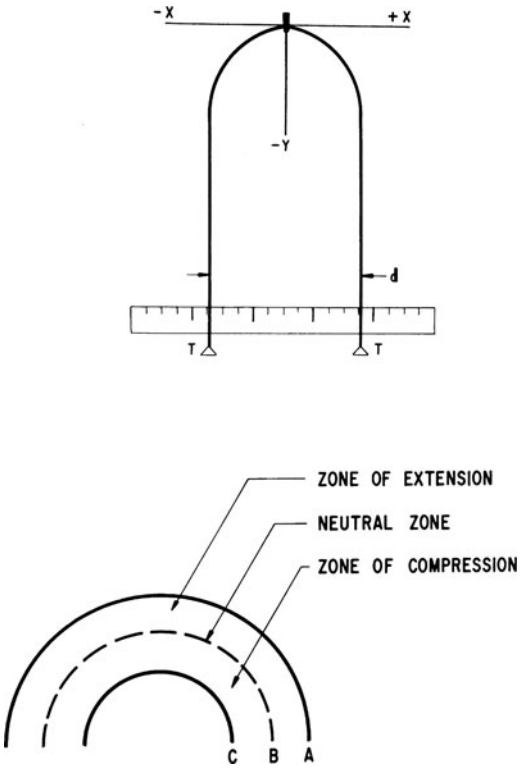

Fig. 9.15 Schematic diagram of the hanging fiber bending test [49, 89]. *Top*: Hair fiber photograph in the bending test. *Bottom*: Schematic of a bent hair fiber

feel, to combing forces and to hair breakage. See the section near the end of Chap. 10 for details.

9.4.1 Bending Methods

Several methods have been described for measuring the bending properties of hair fibers. For human hair, the balanced fiber method of Scott and Robbins [49, 89] appears to be the easiest to handle experimentally (except for very curly hair). This method provides less scatter (lower variances) than the other methods [49]. However, this method is only applicable to hair fibers of curvature Types I and II and possibly some of Type III, but not hairs with higher curvatures.

A newer method developed by Baltenneck et al. [90] involves a bending pendulum of parallel hair fibers. This method also appears to offer promise for determining the bending properties of hair fibers [90]. Baltenneck's method most likely could be used with hairs with higher degrees of curvature than the Scott and Robbins method.

The vibrating-reed method (oscillating fiber cantilever) has also been used with human hair [10]. The cantilever beam method [89], the loop deformation method [91], and the center load beam method [92] have also been described for textile fibers.

The method of Scott and Robbins involves attaching small equal weights to each end of the fiber. Each end of the fiber is individually threaded through a short length of plastic tubing. A tapered metal pen is inserted in the other end of the tube (the combined weight of pin and tube is known). The fiber is then hung over a fine wire hook and the distance d between the two vertical legs of the hanging fiber is measured (see Fig. 9.15).

The distance d is an index of stiffness of the fiber. The stiffness coefficient G (ratio of applied force to bending deflection) may be calculated from d using this expression:

$$G = T\, d^2/8$$

T is the force applied to each fiber leg in dynes ($g \times 980.6\ cm/s^2$).

The elastic modulus for bending E_B may also be calculated from d:

$$E_B = \frac{\prod Td^2}{2A^2}$$

A is the fiber cross-sectional area, determined from diameter or linear density measurements.

Scott developed an equation that describes the hanging fiber shape by conventional X, Y coordinates and the d measurement. We have verified this equation by

showing that calculated fiber shapes are exactly superimposable on those of enlarged photographs of actual balanced hanging fibers (see Fig. 9.15).

The bending modulus E_B by this method at 62% RH and 75°F is approximately equal to Young's modulus for stretching (E_s) determined under similar experimental conditions by the load–extension method, $E_B = 3.79 \times 10^{10}$ dynes/cm^2 or 3,790 MPa. These values have not been corrected for fiber ellipticity. Such a correction may be considered academic, but it should make E_B slightly higher than E_s for human hair, because elliptical fibers orient to bend over their minor axis in this method.

Simpson's [10] values of E_B for human hair were higher 5.35×10^{10} dynes/cm^2 or 5,350 MPa. However, Simpson used the vibrating cantilever method. This procedure produces E_B values that vary with vibration frequency. Simpson also used a lower RH (50%).

The stiffness index of hair fibers by the method of Scott and Robbins provides falling curves when plotted against weight attached to the fibers. Routine measurements are made at 0.2 g total weight (0.1 g per fiber leg), and with a wire hook of 0.77 mm diameter (0.19–1.28 mm). For fine fibers, <50 μm in diameter, smaller weights (0.05 g per fiber leg) are recommended. (For additional details, see references 49, 89.)

9.4.2 *Stiffness and Linear Density*

The stiffness coefficient is directly proportional to fiber linear density. The data plotted in Fig. 9.16 provide an index of determination of 0.94 [49] demonstrating that 94% of the variation in stiffness (in this experiment) is accounted for by

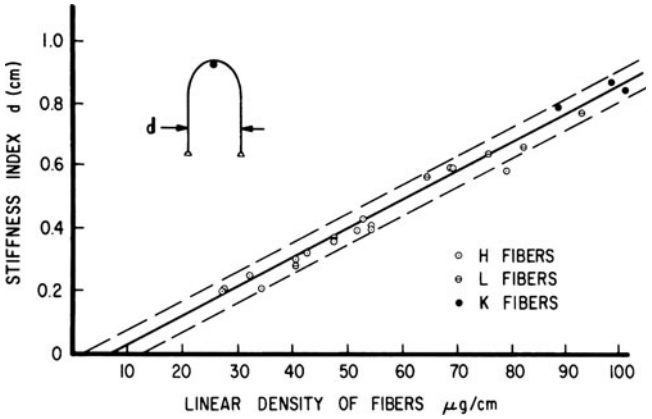

Fig. 9.16 Hair fiber stiffness index and linear density [49] (reprinted with permission of the Journal of the Society of Cosmetic Chemists)

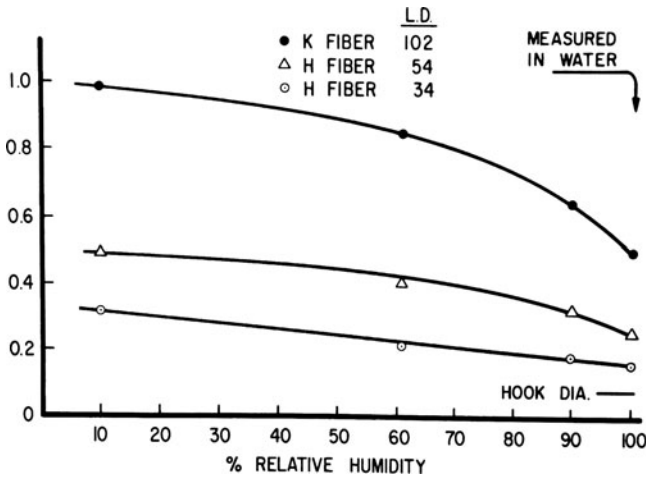

Fig. 9.17 Hair fiber stiffness versus relative humidity [49] (reprinted with permission of the Journal of the Society of Cosmetic Chemists)

variation in linear density. Therefore, consistent with theory, stiffness increases with fiber diameter. Theory predicts a fourth power dependence between fiber stiffness and diameter for a perfectly elastic system.

9.4.3 Stiffness and Relative Humidity

As one might anticipate, hair fiber stiffness also varies with RH. It decreases with increasing RH as shown by the Scott and Robbins method (see Fig. 9.17). We might conclude that hair fiber stiffness generally parallels fiber-stretching properties with respect to treatments. This conclusion is probably correct in most instances.

As indicated above, a novel approach to determining the bending properties of hair fibers was published by Baltenneck et al. [90] in which a bending pendulum composed of 39 parallel hair fibers, each 11 mm long and spaced 1 mm apart are fixed on a metallic support. The pendulum is then set into motion and the hair bending stiffness is assessed by the number of strokes observed until the pendulum stops. The data from this method on the effects of RH on bending stiffness agrees with that of Scott and Robbins [49], that is, the bending properties of hair decrease with increasing RH.

9.4.4 Bending Stiffness and Hair Damage

Baltenneck et al. [90] examined the bending properties of virgin and chemically damaged hair fibers. Their results show that virgin hair is less stiff than either

bleached (peroxide/persulfate bleach for 50 min) for most dry state conditions (20–80% RH). But, virgin hair is stiffer than permanent waved hair at 100% RH. Surprisingly, bleached hair did not show a difference in stiffness from virgin hair at 100% RH. This latter result is not consistent with results of Scott and Robbins.

9.4.5 Bending Stiffness and Hair Fiber Curvature

Elliptical fibers bend over their minor axis and most human hair fibers are elliptical rather than circular. Nagase et al. [93] found a statistically significant correlation of curl radius (Curl types I to IV) with ellipticity among hair from 132 Japanese women. However the index of determination was only 0.06 meaning that the ellipticity decreases only very slightly as the curl increases for relatively straight hair, that is only 6% of the variation in ellipticity could be explained by the curl radius. Therefore, from ellipticity effects alone, we would not expect a meaningful impact of hair fiber curvature on the bending properties of Asian type hair over the range of curvatures from Curl type I to IV. No large studies were found comparing curvature and ellipticity for Caucasian hair over Curl types I to IV.

However, African type hair is different. Porter et al. [47], from data on 12,050 hair fibers, found that African type hair becomes more elliptical with increasing hair fiber curvature ($R^2 = 0.947$). Therefore, 95% of the variation of ellipticity in African type hair can be explained by hair fiber curvature for curly hair. In addition, Porter et al. demonstrated that the cross-sectional area of African hair decreases with increasing fiber curvature. Elliptical ratios above 1.6 are common for African hair [47]. Therefore, other variables being equal we would expect the bending stiffness index to decrease with increasing hair fiber curvature for African type hair over the curvature range of curl types IV to VIII.

In contrast to the bending stiffness index, the bending modulus is a constant, calculated by dividing by the 4th power of the fiber diameter (diameter of minor axis). As indicated earlier, we know from work by Thibaut et al. [94] that the IF's and KAP's of the cortex of human hair become more asymmetrically distributed with increasing fiber curvature for African [94], Caucasian [94] and Asian hair [95]. This effect was demonstrated for Asian hair by Bryson et al. [95] resulting in different IF arrangements concentrated in the concave part of the curl versus the convex part of a curl, see Chap. 1 for details. Therefore the bending modulus should change with increasing hair fiber curvature because of the changing arrangements of these cortical structures with curvature.

9.4.6 Bending and Possible Cuticle Contributions

There is evidence that the cuticle also plays a role in the bending properties of keratin fibers as shown by Kawabata et al. [96] on wool fiber and by Masaaki [97],

Swift [98] and by Atushi et al. [99] on human hair fibers. Hadjur et al. [100] described a lack of symmetry in the number of cuticle cells near the minor axis versus the major axis of elliptical African hair fibers. A lack of symmetry in the cuticle of curly African type hair fibers versus greater symmetry for straighter hair of Asians and Caucasians should affect the bending and torsion properties. Nevertheless, I have not been able to find any studies relating hair fiber curvature to the bending properties of hair fibers.

9.5 Torsion and Fiber Rigidity

Hair fibers are routinely twisted during combing, brushing, and setting; however the extent of twist is relatively small compared to the twist required to break a fiber. The resistance to twisting is the torsional rigidity. By definition, rigidity is the torque required to produce a twist of one turn per centimeter [91]. Rigidity in twisting is analogous to stiffness in bending and is a fundamental property to hair fibers. Furthermore, torsion and fiber swelling methods measure stresses and therefore bonding perpendicular to the fiber axis better than any other method.

9.5.1 Torsion Methods

Several methods have been described for determining the torsional rigidity and the torsional modulus (modulus of rigidity) of hair and/or textile fibers [8, 37, 101–107]. Basically, these methods are related to the torsion pendulum method [8, 102, 105, 107]. The torsion pendulum method involves suspending a small pendulum from a fiber. The fiber is then set into free rotational oscillation. By determining the period (P) of oscillation (time of vibration, which generally averages 10–20 complete oscillations), the fiber length (L), the fiber diameter (D), and the moment of inertia of the pendulum (I), the torsional modulus E_T may be calculated.

$$E_T = \frac{128\ \Pi I L}{P^2\, D^4}$$

The rigidity R (resistance to twisting) may be calculated from this expression:

$$R\ = 8\Pi^3 I\ L/P^2$$

And the rigidity is related to its modulus by:

$$E_T = \ R\ /\ J A^2$$

A is the fiber cross-sectional area and J is a shape factor, usually assumed to be 1 for human hair and wool fiber.

Another useful torsion parameter is the logarithmic decrement (δ). This parameter describes the decay in amplitude of the untwisting pendulum with successive oscillations:

$$\delta = (1/n)\ \ln(a_1/a_n)$$

n = the number of oscillations and a_1 and a_n are the amplitude of the first and the nth oscillation. This logarithmic decrement is an indication of the torsional elasticity of the system. When δ = 0, the fiber is perfectly elastic, and as δ increases the fiber becomes less elastic. The logarithmic decrement is related to the torsional loss modulus ($E_{T'}$) in the following manner:

$$E_{T'} = E_T \delta / \Pi$$

A major drawback to the simple torsion pendulum method was that it could not be used while the fiber is immersed in liquids because of the damping effect of the liquid. However, Wolfram and Albrecht [107] devised a very clever scheme to overcome this obstacle by inserting the fiber into a small glass capillary tube, thus permitting the torsional properties of hair fibers (and other fibers) to be measured in both air and liquids. Other methods are available [103, 104, 108] for measurement of the rigidity of fibers immersed in liquids. For additional details, see the references indicated and the texts by Meredith and Hearle [108] and Morton and Hearle [92].

9.5.2 *Rigidity and Moisture*

The torsional modulus for human hair by the pendulum method is lower than either the stretching or the bending modulus at 60–65% RH. But more importantly, water has a greater effect on torsional properties than on either stretching or bending for both human hair and wool fiber (see data describing these three different elastic moduli: Tables 9.5 and 9.6).

For wool fiber the effect of water on the torsional properties is almost 3–4 times as great as on the bending or stretching properties, whereas for human hair the

Table 9.5 Comparison of the stretching, bending, and torsional moduli for human hair at 60–65% RH [106] (Scott, private communication)

E_S	E_B	E_T
3.89×10^{10}[a]	3.79×10^{10}[a]	0.89×10^{10}[a]
3890[b]	3790[b]	890[b]

[a]These values are dynes/cm^2. E_B and E_S were determined at 62% RH and room temperature

[b]These values are in MPa

Table 9.6 Influence of moisture on stretching, bending, and torsional moduli

	E_S		E_B		E_T	
	0% RH/ 100% RH	65% RH/ 100% RH	0% RH/ 100% RH	65% RH/ 100% RH	0% RH/ 100% RH	65% RH/ 100% RH
Human hair	–	2.62 [30]	3.8[a]	2.4[a]	–	4.1 [103]
Wool fiber	2.76 [25]	2.58 [33]	–	–	16.1 [33]	9.2 [33]

[a]Calculated from unpublished data by Dr. G.V. Scott

effect is nearly a factor of 2 between 65% and 100% RH (see Table 9.6) and it should be much greater from 0% to 100% RH.

Wolfram and Albrecht [107] found that the logarithmic decrement varies with fiber diameter. This parameter decreases with increasing fiber diameter in water, but it does not vary with diameter at 65% RH. This finding suggests that in water, the hair is less elastic or more plastic. These scientists implicate the cuticle as primarily responsible for this increase in torsional plastic behavior for human hair in water and as shown later in this section; cuticle effects on the torsional behavior of hair fibers are measurable in contrast to tensile effects.

9.5.3 Torsion and the Cuticle and Elliptical African Hair

Masaaki [97] examined the torsional modulus of rigidity on both intact hair and hair in which the cuticle was removed by rubbing. His results demonstrated that the cuticle is about 3.5 times as rigid as the cortex. Therefore, the cuticle plays a major role in the twisting properties of human hair fibers. These results are in agreement with a similar study on wool fiber by Kawabata et al. [96] who examined the bending and shear properties of wool fiber in which the scales were removed by chlorine treatment. Kawabata et al. found that the shear modulus of wool without scales decreased significantly, demonstrating that the cuticle does contribute to shearing effects in hair fibers.

Persaud and Kamath [8] demonstrated that the shear modulus decreased with increasing cross-sectional area for European dark brown hair. Since the ratio of cuticle to cortex increases as hair becomes finer, these scientists concluded that the cuticle is highly involved in the torsional properties of hair fibers. Since the cuticle to cortex ratio also decreases as hair diameter increases, these scientists conclude that the rigidity of the cuticle dominates this measurement. Their data also showed a large increase in energy dissipation for fine to medium hairs after saturation with water and they concluded that the cuticle to cortex ratio plays less of a role for a coarse fiber's energy dissipation in the wet state. These authors interpreted this effect as a contribution of the high cuticle to cortex ratio in large log decrement values for the fine fibers versus the corresponding values at 65% RH.

As indicated, Dankovich et al. [43] demonstrated that twisting highly elliptical hairs even at low twist levels produces cuticular damage with scales compressing into one another from "tangential compression". This cuticle damage was less in more circular hairs. Since Porter et al. [47] showed that ellipticity increases with increasing fiber curvature from Curl type VI to Curl type VIII ($R^2 = 0.95$), we would expect that this type of cuticle damage from twisting will increase with increasing fiber curvature for African type hair. African hair often contains natural twists; therefore, twisting hairs with natural twists should be even more complicated. Such an effect has not been reported in the literature.

9.5.4 Torsional Behavior of Damaged Hair

Bogaty [106] examined the torsional properties of permanent-waved and un-waved hair. His results, summarized in Table 9.7, suggested that waved hair is more rigid at low RH and less rigid above 90% RH than un-waved or virgin hair. Wolfram and Albrecht [107] examined the torsional behavior of permanent-waved, bleached, and dyed hair. These scientists confirmed the finding of Bogaty that permanent waved hair (reduced hair) is less rigid than chemically unaltered hair in the dry state. These same scientists also found that the rigidity ratio ($R_{water}/R_{65\%\ RH}$) is lower for bleached hair than for dyed hair, consistent with the greater amount of disulfide bond cleavage by bleaching as compared to permanent dyeing.

If one takes ratios of the dry to wet torsional modulus in Table 9.7, it is apparent that there is a greater effect of moisture on the torsional properties of waved hair than on the torsional properties of chemically unaltered or virgin hair.

The torsional behavior of hair, more than the tensile behavior, is dependent on the cuticle or the external layers of the fiber because of greater shear forces in the periphery versus the center of the fiber during twisting. Torsional behavior is also more sensitive to water than tensile properties. Permanent waves and bleaches do change the torsional properties of hair, as demonstrated by Wolfram and Albrecht. Therefore, torsional methods should prove one day to be more sensitive to cuticle damage than current tensile methods.

Persaud and Kamath [8] used their torsional pendulum method to examine damaged hair and the performance of several hair care active ingredients including

Table 9.7 Torsional moduli of waved and un-waved hair from data of Bogaty [106]

% RH	Unwaved hair MPa	Waved hair MPa
41	1,190	1,250
58	1,060	1,130
65	890	990
81	730	760
93	420	400
100	220	140

a cationic surfactant, a conditioning polymer and hair spray films. These scientists also used the elliptical cross-section of hairs instead of assuming circularity to calculate torsional rigidity to refine their torsional data. Persaud and Kamath found that the torsional properties of hairs treated with hair spray dissipate more energy versus un-treated hairs. Persaud and Kamath suggested that the hair spray polymer is softer than the cuticle and deforms more than the cuticle thus energy dissipation is higher for hair spray treated fibers.

Persaud and Kamath [8] also examined the effects of a cationic polymer (Polyquaternium-10) and of a cationic surfactant (Cetyl trimethyl ammonium bromide) on bleached hair in this same study. Bleaching significantly reduces the shear modulus at 65% RH due to oxidation of disulfide bonds to cysteic acid and the subsequent additional water absorption in the hair (particularly in the rigid cuticle layers and in the matrix of the cortex). Treatment of the bleached hair with the cationic polymer produced a small increase in the shear modulus and in the average log decrement values confirming a detectable effect of ingredients on and in the surface layers of the fibers.

Treatment of bleached hair with 0.5% of the cationic surfactant produced a large increase in the shear modulus and a significant reduction in the average log decrement values relative to the bleached controls. This stronger effect is probably due to penetration of the surfactant into the cuticle layers and perhaps even into the cortex as opposed to the cationic polymer which is confined more to the surface of the fibers.

Thus Persaud and Kamath [8] demonstrated the sensitivity of the torsional method to all three of these hair treatments that act predominately on and in the cuticle; whereas tensile measurements did not show any significant changes with these same treatments confirming that tensile properties are a property of the cortex [7] and that torsional measurements are more sensitive to effects on and in the cuticle and to effects involving changes in water content of the total fiber.

9.5.5 Damage to Hair by Twisting

Twisting hair and twisting and stretching hair is described in the section entitled *Twisting and Stretching Normal Hair and Hair with Natural Twists* in this chapter.

9.6 Density of Hair (Mass/Volume)

The density of human hair in solutions of benzene-carbon tetrachloride was determined by the method of Abbott and Goodings [109]. The density of chemically unaltered hair at 60% RH varied from 1.320 to 1.327, depending on lot (dark brown European hair from DeMeo Bros., New York, and three samples taken from heads of volunteers). The density of our wool control was 1.320, identical with one lot of

Table 9.8 Variation in the density of wool fiber with RH [110]

% RH	Density
0	1.304
15	1.3135
25	1.3150
68	1.3125
85	1.304
94	1.2915
100	1.268

hair. Permanent waving did not change the density of hair. Bleaching (approximately 25% disulfide rupture) increased it, but only by 0.45%.

King [110] determined the density of wool fiber as a function of RH. Some of King's results are summarized in Table 9.8. King's data show that density changes are negligible for wool fiber from 15% to 85% RH or normal room humidity. One would expect the density versus RH relationship for wool and human hair to be similar, since their densities at 60% RH and their moisture binding versus RH relationships are virtually identical as demonstrated later in this chapter. Hearle and Peters [111] explained that the increase in fiber density with moisture regain from 0% to 15% RH is contrary to expectations and is not fully understood.

The objective of these density experiments was to determine the relative density of human hair and wool fiber and the influence of damaging cosmetic treatments on this important property. The results of these experiments confirm the conclusions of several others [91, 112]: the densities of human hair and wool fiber are similar, and there is no appreciable change in the density of human hair from permanent-waving or bleaching treatments.

9.7 Dimensions, Swelling and Effects of Fiber Shape on Reactivity

Two of the most commonly measured hair fiber dimensions are length and diameter. Assuming that a hair fiber approximates a cylinder, its volume, cross-sectional area, radius, and surface area may be obtained from formulae that describe the volume of a cylinder ($V_{cylinder}$), the area of a circle (A_{circle}), and the surface area of a right cylinder ($S_{cylinder}$), in terms of its diameter (D) and length (L).

$$V_{cylinder} = 0.7854\,D^2\,L$$
$$A_{circle} = 0.7854\,D^2$$
$$S_{cylinder} = D\ \Pi\ L$$

Although human hair fibers vary in cross-sectional shape, from nearly circular to elliptical and even "triangular", normalizing for most elastic and other properties to

fiber coarseness can significantly reduce experimental scatter. A convenient equation for calculating the cross-sectional area of an ellipse is:

$$A_{ellipse} = \pi R_1 R_2$$

where R_1 is the radius of the maximum diameter and R_2 is the radius of the minimum diameter.

Whenever maximum and minimum diameters are given one may calculate the average diameter from the following equation:

$$D_{average} = \sqrt{D_{maximum} \times D_{minimum}}$$

Fiber thickness is usually characterized as fiber diameter or cross-sectional area. Corrections to diameter for ellipticity are often not employed and are usually not required except for highly elliptical hair fibers. Hair fiber dimensions are also necessary to calculate fundamental elastic properties, and dimensional changes are often employed to follow the course of chemical reactions with hair.

For measurement of short lengths of hair fibers (in the millimeter range or less) a microscope may be used, but for longer lengths (several centimeters or longer) a cathetometer is useful. Although fiber diameter may be measured directly with a microscope, or more crudely with micrometer calipers, other excellent methods are available for determining cross-sectional dimensions of human hair. More recently laser scanning equipment has been employed similar to the system described by Li and Tietz [113]. This approach should improve the precision of the measurements over microscopy especially when averaging over large sections and large numbers of fibers.

9.7.1 Methods to Determine Hair Fiber Dimensions

Both single-fiber and multiple-fiber methods are available for determining hair fiber cross-sectional dimensions or changes. Single-fiber methods include linear density, microscope (light or electron), vibrascope, micrometer caliper, and laser beam diffraction. For multiple-fiber determinations, a centrifuge and optical scanning devices may be used.

9.7.1.1 Linear Density Method

The linear density method is one of the methods of choice, for determining hair fiber coarseness (diameter). A fiber is cut to a given length (10 cm is convenient), conditioned at 55–65% RH, and weighed on a microbalance sensitive to 2 μg or

better. This gives the fiber weight in g/cm, which is divided by the fiber density, 1.32 g/cm^3, to obtain the cross-sectional area in cm^2 (A).

$$A = \frac{g/cm}{1.32}$$

The area so calculated is independent of cross-sectional shape. The fiber diameter (D) may then be calculated, assuming circularity:

$$D = \sqrt{A/0.7854}$$

The volume (V) in cm^3 for a given weight (M) of hair may be calculated from the fiber density:

$$V = M/1.32$$

Finally, the length (L) of a fiber of volume V and radius r may be rechecked (since it is precut at a specified length and measured):

$$L = V/r^2\Pi$$

The length may then be used to estimate the surface area (Su).

$$Su = 2\Pi r\ L$$

This scheme assumes that the density of all hair fibers is the same. It requires a minimum of manipulations and is an excellent "averaging technique" for dry state dimensions of hair fibers. Cross-sectional area and volume estimates for circular and elliptical fibers should be relatively accurate, as well as diameter and radius for round fibers. This method does not provide an indication of ellipticity, but provides an average diameter with respect to length as well as to cross section (average diameter, not maximum or minimum diameter). The deviation of fiber diameter with increasing ellipticity is described in Table 9.9 which shows only about 1% difference in cross-sectional area by assuming circularity or a regular ellipse from 40 to 120 microns and from an elliptical ratio of 1.10–1.78.

9.7.1.2 Microscopic Method

Several excellent papers [114–116] describe experimental details for measuring the diameter of human hair fibers with a light microscope. Once the diameter is obtained, calculation of radius, cross-sectional area, volume, and surface area may be made as described in the previous section.

Table 9.9 Deviation of the diameter of a circle from the major and minor axes of an ellipse

Area assume	Average D assuming	Ratio D_1/D_2[a]							
Circle μm^2	Circularity μm	1.108		1.234		1.500		~1.78	
		D_1	D_2	D_1	D_2	D_1	D_2	D_1	D_2
1,257	40.0	42	38	44	36	49	32.7	53.3	30
Ellipse area		1,253		1,244		1,258		1,256	
11,310	120.0	126.3	114	133.3	108	147	98	156.5	92
Ellipse area		11,308		11,307		11,314		11,308	

D_1 = major axis of ellipse, D_2 = minor axis of ellipse and R1 and R2 = radius in μm

[a]Calculations above assume that the cross-sectional shape is that of a regular ellipse and these equations were used for the average diameter and area of an ellipse:

$D_{average} = \sqrt{D_{maximum} \times D_{minimum}}$ and $Area = R_1 \times R_2 \times \pi$

The light microscope is an excellent instrument for determining dimensional changes in hair fibers while they react with either liquid or gaseous systems (including moisture in air). The light microscope can also be used to measure deviation from circularity; although, extensive manipulation and multiple measurements (10–20) along each fiber's axis are required for accurate measurement. A modern scanning electron microscope, with vernier, is also a useful instrument to measure dry state (approximately 0% RH because of evacuation) diameter of human hair fibers.

9.7.1.3 Vibrascopic Method

The vibrascope [117, 118] is a device that applies an oscillatory force of known frequency to a filament under tension. The fiber cross-sectional area (A) in cm^2 may be computed from the lowest (natural) frequency (f) in cycles per second that produces mechanical resonance. The tension (T) on the fiber is in dynes, the fiber length (L) is in cm, and its density is 1.32 g/cm^3.

$$f_i = \frac{1}{2\,L}\sqrt{T/1.32\,A}$$

The fiber diameter, radius, volume, and surface area may then be calculated as described.

This method assumes that the fiber is a homogeneous filament and provides an average diameter. Nonetheless, it has been shown by Montgomery and Milloway [117] to be in close agreement with microscopic measurements of the diameter of nylon fibers. The vibrascopic method, like the linear density method, is an excellent averaging technique and offers time advantages over microscopic methods.

9.7.1.4 Micrometer Caliper Method

This method works well for hard fibers like steel, tungsten, and glass, but not as well for softer fibers like human hair. It is a crude but fast way to approximate hair fiber diameter. Since hair fibers yield to low compression forces, and these forces are difficult to control, the micrometer caliper technique tends to provide low values for fiber diameter and a large variance.

9.7.1.5 Sieving Hair Fibers

Busch [119] used fine-mesh sieves to separate fine hair fibers from a bundle for further characterizations. It is conceivable that further separations of hair fibers may be achieved via sieving and average diameters approximated via this useful technique.

9.7.1.6 Laser Beam Diffraction Method

Brancik and Datyner [120] described the diffraction of monochromatic light from a laser to measure the diameter of single wool fibers in liquids. Busch [119] used a laser beam diffraction system with robotic control for characterizing hair fiber diameter and shape for a large number of hair fibers. Also, see the paper by Li and Tietz [113].

9.7.1.7 Centrifuge Method

The centrifuge method has been described by Valko and Barnett [74] and by Barnett [121]. This method involves treating a known weight of parallel fibers (400–800 mg and approximately 20 cm long) with a liquid, centrifuging to remove excess liquid between the fibers, and reweighing. This is a good averaging technique for multiple fibers and is well suited to follow reactions with hair fibers by measuring the percentage weight gain of liquid imbibed by the hair. This method may be used to approximate fiber volume changes in aqueous systems, since weight gains at different relative humidity correspond relatively well to volume increases (see Table 9.10). From volume changes, cross-sectional area, diameter, length, surface area, and other dimensional changes may be computed (see the section entitled Linear Density Method for details).

9.7.1.8 Optical Scanning Devices for Determining Fiber Diameter

OFDA (optical fiber diameter analyzer) laser scanning as described by Watt [123] was originally developed for the wool industry. However, this method has found

Table 9.10 Percentage weight and volume changes versus RH for wool fiber

	Changes caused by absorption of water		
% RH	% volume [122] increase	% weight [37] increase	% weight [74] increase
0	0	0	0
9	–	3.9	–
10	5.7	–	–
20	–	–	7.6
40	12.2	10.2	–
60	16.3	–	–
63	–	14.8	–
86	–	22.6	–
90	24.6	–	–
100	32.1	31.2	31.1

Table 9.11 Hair fine to coarse and fiber diameter by Courtois et al. [124]

Hair fineness	Fiber diameter (μm)
Very fine	<35
Fine	35–50
Medium	51–65
Thick (coarse)	66–80
Very thick (very coarse)	>80

application for most natural and synthetic fibers including human hair. This method essentially takes images of an array of fibers (several hundred in cross-section) and scans the field with a laser that measures the width or diameter of the exposed fibers that are free from other fibers. Temperature and relative humidity are also recorded at the time of measurement. This method offers time and cost advantages and averages a large number of hairs.

9.7.2 Fine Coarse Hair

Consumers usually evaluate fine or coarse hair by handle or feel; however scientists generally evaluate these parameters by measuring fiber diameter or cross-sectional area. Fine and coarse distinctions are used for qualitative comparisons in the cosmetic industry, but there are no accepted quantitative definitions of these terms analogous to wool fiber. One reference that defined fineness of human hair quantitatively by fiber diameter is by Courtois et al. [124] in a study of ageing and hair cycles. This reference defined hair fineness by the diameters summarized in Table 9.11.

Although such a classification of hair fineness by diameter as in Table 9.11 might be useful in some cases, it describes the average hair of Caucasians and Africans as coarse and the hair of Asians (described below) as very coarse. However, this is not the way we normally classify Caucasian hair. To date, I have

Table 9.12 Fine-coarse wool fibers defined by fiber diameter [111]

Type of wool fiber	Diameter in μm
Ultrafine merino	<17.5
Superfine merino	17.7–18.5
Fine merino	<19.5
Fine medium merino	19.6–20.5
Medium merino	20.6–22.5
Fine	<24.5
Medium	24.5–31.4
Fine crossbred	31.5–35.4
Coarse crossbred	35.5

not been able to find any other reference that used this quantitative classification by Courtois et al. [124].

On the other hand, coarse and fine are more clearly defined quantitatively for the wool industry because the diameter of wool fibers is related to both the end use and to the breed of sheep/animal. Table 9.12 shows definitions for wool fiber diameters expressed as fine or coarse with additional distinctions. In general, wool fibers <25 μm in diameter are used for garments whereas coarser grades are used for outerwear or rugs. Such distinctions for wool fiber are clearly more useful than for human hair; however, some quantitative distinctions for coarse and fine human hair could be useful to the cosmetic industry.

9.7.3 Variation in Fiber Cross-Sectional Shape with Emphasis on Diameter and Ellipticity

9.7.3.1 Fiber Diameter by Geo-Racial Group

The term race applies to sub-populations or groups of people similar in several biological characteristics. In the past, races developed and persisted because travel over large distances was limited, thus, similar peoples interacted and procreated. The geographic or racial differences that are found today in hair and skin type are most likely remnants of prior adaptations to temperature, sun exposure and other environmental influences.

The words ethnic and ethnicity have been misused in the cosmetic industry. Ethnicity relates more to similarities in or shared social customs. Race relates more to similarities in physical characteristics. In the following pages I refer to geo-racial groups linking geographic origin to race. I will try to refrain from using the phrase ethnic hair, but I will sometimes inadvertently use the term geo-ethnic. The cosmetic industry frequently refers to these three primary geo-racial hair types: African type hair originates primarily from south, west, or central Africa and the donors with a few exceptions tend to have heavily pigmented skin. Asian type hair originates from mid-eastern and south East Asia and the donors tend to have light to

medium skin pigmentation. Caucasian hair originates from northern Europe or North Africa and the donors tend to have lightly pigmented skin, but some may have heavily pigmented skin.

These geo-racial groups will be referred to frequently in the sections involving hair fiber shape focusing on fiber diameter, ellipticity and hair fiber curvature. These three geo-racial groups correspond to the Ethiopian, Mongolian and Caucasian groups used in a prior edition of this book. Fiber curvature and cross-sectional shape as well as pigmentation variations of human scalp hair are controlled genetically (Chap. 3) and these fiber shape characteristics control much of the cosmetic and physical behavior of human hair. Therefore, geo-racial information on hair characteristics can and has been useful to the cosmetic scientist, although a century from now it will likely be less useful.

Other classifications such as by curvature type will ultimately become more important to cosmetic science than the three geo-racial groups because curvature is so important to all cosmetic hair assembly properties as discussed in the last part of Chap. 10. Consider the fact that the cosmetic behavior of scalp hair of a Caucasian of Curl type IV hair by the STAM procedure [47] (see the section entitled, *Measuring Hair Fiber Curvature in this Chapter*) has more in common with Curl types IV of the African and Asian groups than with a curl Type I or II of their own geo-racial group. The commonality is in the way their hair behaves with regard to the more important cosmetic hair assembly properties described later in Chap. 10.

During the latter days of this century and the next, populations of Curl types III, IV and V will likely increase and Curl types I and VIII will decrease. So, in the near future we must learn to type hair even better by its physical characteristics and become more quantitative with regard to its relationships to its important cosmetic hair assembly properties. Table 9.13 summarizes the general qualitative characteristics of the scalp hair of the three major geo-racial groups.

It is generally accepted that on average the hair of Africans and Asians is coarser than that of Caucasians [125, 126]. Randebrock [126] suggested that human hair from the scalp varies from 40 to 120 μm in diameter. Kaswell [127] indicated that the diameter of human scalp hair varies from 15 to 110 μm. The lower end of this estimate likely includes infants and children's hair. Yin et al. [112] suggested that Caucasian hair of adults (the finest of the three major races) varies from 50 to 90 μm. Yin is talking about the variation in diameter means of the hair of individuals rather than the total variation among individual hairs among different

Table 9.13 Hair fiber characteristics by geo-racial group

	Fiber characteristics [125, 126]			
Geo-race	Coarseness	Curvature	Cross-sectional shape	Color
Caucasian	Fine	Straight to curly	Nearly round to oval	Blond to dark brown
African	Coarse	Wavy to wooly	Slightly oval to elliptical	Brown-black to black
Asian	Coarse	Straight to wavy	Nearly round to slightly oval	Dark brown to brown-black

See Fig. 9.18

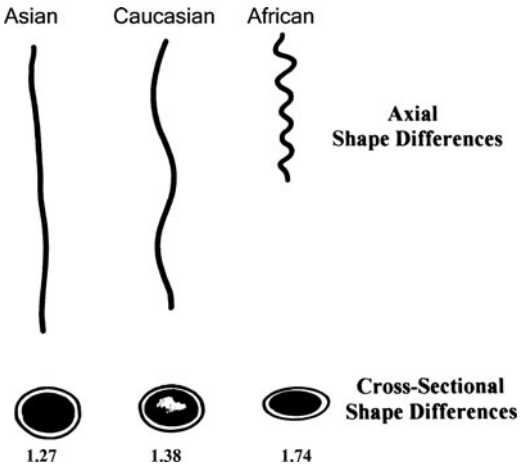

Fig. 9.18 General shapes of human hair of different geo-racial origins

Caucasians. We found slightly greater variation for the means of Caucasian individuals' hair than suggested by Yin et al.

Other sources cite even larger variation for example, Elert [128] cites from 17 to 181 μm. Elert most likely is referring to variation among individual hairs and not mean fiber diameters for individuals, and Elert likely includes minimum to maximum fiber diameter for adult, children's and infants' hair rather than means. For example, Nagase et al. [93] measured maximum and minimum hair fiber diameters on hair from 132 Japanese females ranging from 10 to 70 years of age. The maximum diameters, of 8,926 hairs, varied from 30 to 170 μm averaging 95.3 ± 16.5 μm and the minimum diameters varied from 30 to 130 μm averaging 74.4 ± 10.5 μm.

Table 9.14 summarizes means for human scalp hair diameter by geo-racial group from several references showing that hair from Caucasians is finest and hair from Africans is coarser while hair from Asians is coarsest. For this table, I attempted to use averages from hair of 10 or more persons per group. In a few cases I could not do so. The pooled hair was averages of 10 hairs from each group with hairs from more than one person. The Steggarda and Siebert [129] data used in previous editions was deleted because these scientists used hairs from only five females.

The actual diametric variation of individual hairs must be greater than shown in the distributions of Table 9.14 which are obtained from averaging means of several hair fibers for several subjects. The three largest studies of the data listed in Table 9.14 are the study by Nagase et al. [93] on scalp hair of Japanese females ages 10–70 and the study of Trotter and Dawson [133] on hair of "American whites" and French Canadians [131]. Data was extracted from these two latter studies for females of ages 10–89. Nagase et al. measured and listed maximum and minimum diameters while Trotter and Dawson measured linear densities on the hair of American whites and French Canadians. For French Canadian hair, these scientists also measured maximum and minimum diameters and linear densities from which the calculated diameters compared favorably.

Table 9.14 Mean fiber diameter (MFD) and cross-sectional area of scalp hair of three geo-racial groups (females)

Reference	Asian scalp hair		African scalp hair		Caucasian scalp hair	
	MFD (N)	Area	MFD (N)	Area	MFD (N)	Area
Wolfram [130]	77 (20)	4,657	66 (20)	3,421	72 (20)	4,072
Syed [44]	–		77 (10¥)	4,657	74 (10¥)	4,301
Trotter [131]	–		–		66.8 (154)	3,504
Trotter et al. [133]	–		–		70.5 (120)	3,902
Franbourg [132]	78 (18)	4,804 ± 159	77 (16)	4,274 ± 215	69 (20)	3,857 ± 132
Nagase [93] J	84.2 (132)	5,568	–		–	
Tajima [135] J	83.3 (113)	5,450				
Otsuka et al. [134] J	81.2 (7,585)	5,178				
Otsuka et al.[134] C	80.23 (957)	5,056				
Galliano [136] C	87.2 (19)	5,974			72.5 (16)	4,124
Porter [47]			71.2° (274)	3,979°		
Mean	81.6 ± 3.6	5,241 ± 173	72.8 ± 5.3	4,083 ± 521	70.8 ± 2.6	3,960 ± 275
Total persons	(n = 8,854)		(n = 320)		(n = 340)	
Vernall [137] MEN€	85.1 (n = 20) C	5,688	75.8 (n = 19)	4,513	68.2 (n =21)	3,653
Trotter [133] MEN€					69.0 (131)	3,739

MFD in μm; N = No. persons; Area in μm^2₮

Most of these studies used a microscopic method except for Franbourg [132] and Nagase et al. [93] who used a laser method. The studies by Trotter [131, 133] are calculated from linear densities for females and males ages 10–49. Otsuka and Nemoto [134] did not describe methods. When maximum and minimum diameters were cited this equation was used to calculate the mean fiber diameter $D = \sqrt{d_{max} \times d_{min}}$. ¥ pooled hair, *J* Japanese hair, *C* Chinese hair, €*MEN* ages 20–30 by Vernall [137] and 10 to 49 for Trotter, ₮ represents area calculated by the following formulae: $A = r_1 \times r_2 \times \Pi$ for an ellipse or by A = MFD^2 × 0.7854 for a circle giving essentially equivalent areas otherwise areas are quoted from the paper. °Calculated from relationship by Porter et al. [47] for Curl Class and Area and the average Curl Class for African hair

Table 9.15 Approximate scalp hair diameters by race/country for females (ages 10–89) [134]

	Asian		Caucasian	
	Japan (J) + China (C)	Japan + China + Thai	USA Eur. + Am	W. Germany
Approx. D (μ)	~81	~79	~53	~58
N	8,537	16,380	574	595

[a]Actual, averages were not given in this paper. The above diameters are estimates of diameters rounded off from midpoints of bar-graphs [134]. It is unfortunate that the actual data with statistics, sampling details and measuring methods were not published in this very large and useful study

The percentage standard deviations of the data of the two studies by Trotter and the one by Nagase were similar and close to 17% which was used to estimate the likely range of means from individual persons for each of the three geo-racial groups. These estimates for Asian hair, 54–110 μm, for African hair 48–96 μm and 46–94 μm for Caucasian hair. This is a much more conservative and very different estimate than the 95% confidence intervals for the actual data of Table 9.14 which is for Asian hair 84.9–78.3 μm and 78.99–64.51 μm for African hair and 72.99–68.6 μm for Caucasian hair. The 95% confidence interval is actually the range within which the actual mean of that data is likely to reside at the 95% level.

The study by Otsuka and Nemoto [134] was the largest study found in the literature for human hair diameters (Table 9.15). This paper did not describe details of how the hair was obtained or measured. The data of Table 9.15 shows that the Asian hair sampled was coarser than the Caucasian hair examined. These data also show that sampling or the actual populations chosen to represent either the Asian or Caucasian hair groups can have an influence on the dimensions found. For example hair from females in Japan and China provided a slightly larger diameter than hair from females from Japan, China and Thailand combined.

The diameter estimates for the Asian hair in this study by Otsuka and Nemoto are close to those of the averages of the studies of Table 9.14; however the estimates for the Caucasian hair are considerably lower than those found for Table 9.14. Otsuka and Nemoto suggest about a 30 μm difference between Caucasian hair and Japanese hair, but the data of Table 9.14 suggest about half that difference. I conclude that part of this difference (between Otsuka and Nemoto data and the data of Table 9.14) is from real diametric differences and part to sampling, scalp site and to un-described methodology [134]. For example, Trotter and Dawson [131, 133] found that hair of French Canadians (N = 136) was 4 micrometers coarser than hair of European "white Americans" (N = 183). In the data of Table 9.15 we see a similar difference for the two Caucasian groups, but part of this difference may also be due to experimental variation.

Trotter and Dawson found that the hair of the French Canadians was darker in color than that of the Americans which could be due to differences in physical characteristics resulting from genetics and in this case related to geographical distribution of the different Caucasian populations. For example, the Trotter and Dawson data may include hair of northern Europeans (American whites) versus southern Europeans (French Canadians), a difference which is frequently

Table 9.16 Calculated maximum D and minimum D and cross-sectional areas for Asian, African and Caucasian hair

Hair type	Ave D	Max D	Min D	Elliptical ratio[a]	Cross-sectional area	Ave. curl type
Asian	82	93.4	72.7	1.28[a]	5,333	II
Caucasian	70	82.8	60	1.38[a]	3,902	II, III
African	72	93.6	55.8	1.68[a]	4,104	IV to VIII

Diameter values in μm and area in μm^2 (average D is from Table 9.14)
All other values calculated from these equations via iteration

$$\text{Elliptical Ratio} = \text{Max D}/\text{Min D}$$

$$\text{Ave D} = \sqrt{\text{Dmax} \times \text{D min}}$$

$$\text{Cross - sectional area} = \pi\ \text{Rmax} \times \text{Rmin}\ (\text{R} = \text{radius})$$

[a]See Table 9.17 for references on elliptical ratios

speculated and described for a limited number of individuals hair, but for which I could not find a large supporting study.

Frequency graphs for each group of women in the study by Otsuka and Nemoto [134] approximate a Gaussian distribution. Random sampling of large groups of women in most populations likely are similar provided ages are limited from about 10 to 60. When a large percentage of older persons are included, especially older men, the distributions will tend to deviate from Gaussian; see the section in this Chapter entitled, *Hair Diameter of Males versus Females*. Table 9.16 was constructed primarily from calculations to approximate the average maximum and minimum diameters and cross-sectional areas from the three major geo-racial groups. Whether one calculates cross-sectional areas assuming circularity or a regular ellipse the results are within 1% of each other (see Tables 9.9 and 9.16).

A discussion of how hair fiber diameter varies with age is described in this chapter in the section entitled, *Fiber Diameter, Cross-sectional Area, Fine Coarse Hair and Hair Growth*.

9.7.3.2 Hair Fiber Diameter and Ellipticity Variation Along the Fiber Axis or Length

In 1942, Seibert and Steggerda [138] examined long hairs cut from the scalps of 7 Caucasian and 9 Mayan females. They selected the longest 80–100 hairs averaging 40–50 cm long and measured maximum and minimum diameters on these fibers sectioned at 2, 10, 20, 30, and 40 cm from the original cut near the scalp. In all but 3 of 16 cases the hairs were larger in area and maximum diameter at their terminal or distal end than at the basal cut. This effect is significantly different by the non-parametric sign test. In addition, the ellipticity (major to minor axis of the diameter) tended to decrease in the direction toward the scalp.

About 50 years later, Hutchinson and Thompson [139] reported changes in the major-axis diameter of human scalp hairs that they associated with changes occurring inside the follicle, during the growth of human hairs. Hutchinson and Thompson concluded that hair fibers do not grow as uniform cylinders. But, they

hypothesized that from the distal end of each hair fiber for a distance toward the scalp of about 6–8 cm an increase in diameter occurs that they associated with the start up of anagen (approximately 5–7 months growth). After that distance of 6–8 cm, their data showed a gradual decrease in the major-axis, but not the minor axis of the fiber. The overall effect from that point is a gradual decrease in fiber ellipticity, cross-sectional area and diameter of each hair shaft.

When reading this paper, I was skeptical because the authors miscalculated cross-sectional areas by a large factor and they hypothesized in some instances without data. But after reading the previous paper by Steggarda and Siebert [138] and the following paper by Nissimov and Elchalal [140] I came to accept the gradual decrease in the major axis from the distal end of the fiber.

Nissimov and Elchalal [140] confirmed this effect and they observed the opposite effect during pregnancy. That is during pregnancy the major axis of the fibers increased from distal to proximal end by 4.5% through 35 weeks of pregnancy. This study was conducted on 15–20 hair fibers each from 13 non-pregnant women (average age 36 years) and 12 post-term pregnant women (average age 29 years). The major axis of the hair fibers in the control group of non-pregnant women during this same 35 week period decreased from distal to proximal end by 5.2%. The decrease in the major axis of hair fibers from only 4 Caucasian non-pregnant women observed by Hutchinson and Thompson was 16.4%. Only a small (likely non-significant) increase of 2.5% was observed in the minor axis on these same hair fibers.

Such variation within each hair fiber helps to explain the wide variation that we observe in maximum and average fiber diameters and ellipticity and when considered with variation among individual hairs on a head and between heads why large sample sizes are necessary to provide meaningful data when measuring hair fiber diameter parameters.

9.7.3.3 Ellipticity of Human Scalp Hair by Geo-Racial Group

Table 9.17 shows that hair from Africans has a greater deviation from circularity (average major axis to minor axis D_1/D_2 of 1.74) than hair from the other two geo-racial groups and compares favorably with the calculated value of Table 9.16.

The hair from Asians is the most circular with an average elliptical ratio of 1.27 and for Caucasians, this ratio is 1.38 and is very close to be calculated values of Table 9.16. These data suggest that the calculated circular diameter for Asian and Caucasian hair averages about 13% and 16%, respectively, from the major and minor axes of noncircular fibers. Therefore, in most circumstances, the assumption of circularity is an acceptable approximation. However, this deviation averages about 26% or greater for most African hair. So, the assumption of circularity for African hair should be carefully considered.

The confidence intervals above in Table 9.17 suggest that there is a 95% probability that the true mean is within this interval. The distributions of the individual geo-racial groups are normal and the Asian, African and Caucasian means are all significantly different by parametic and non-parametric statistics.

Table 9.17 Ellipticity of hair fibers from three geo-racial groups

Source	Asian		African		Caucasian	
	Mean (N)	Range	Mean (N)	Range	Mean (N)	Range
Steggarda [129]	1.25 (10)		1.65 (9)	1.25–2.05	1.35 (10)	
Wolfram [130]	1.29 (20)	1.21–1.36	1.84 (20)	1.67–2.01	1.49 (20)	1.43–1.56
Syed [44]	–		1.83[a]	1.69–2.09	1.29[a]	1.06–1.52
Vernall [137]	1.23 (20) J		1.69 (19)		1.44 (21)	
Franbourg [132]	1.23 (5)	1.16–1.28	1.78 (14)	1.67–1.85	1.32 (11)	1.25–1.39
Nagase [93] J	1.28 (132)	1.02–2.19	–		–	
Porter et al. [47]	–		1.67 (241)			
Mamada et al. [141] J	1.28 (38)				1.40 (35)	
Galliano et al. [136] C	1.31 (19)				1.40 (16)	
Trotter [131]					1.36 (340)	1.09–2.13
Trotter et al. [133]					1.36 (300)	
MEAN	1.27		1.74		1.38	
ŦConfidence Interval	1.239–1.296		1.655–1.831		1.332–1.426	
ŁEstimated Ranges	1.02–2.19		1.25–2.09		1.06–2.13	

Ellipticity is D_{max}/D_{Min}; No. persons = (N)
[a]Pooled hair, *C* Hair from Chinese, *J* Hair from Japanese
Ŧ Confidence intervals suggest a 95% probability that the true mean is within this interval
Ł Estimated ranges suggest the variation in ellipticity found among individual hairs

The estimated distributions suggest variation in ellipticity found among individual hairs from the data by Nagase [93] and by Trotter [131, 133].

The study by Nagase et al. [93] contained 132 Japanese females ages 10–70 and a total of 8,926 hairs were measured for maximum and minimum diameter. Therefore, this study is the most reliable with respect to the range of ellipticity for individual hairs (not means) for this geo-racial group, which varied from 1.02 to 2.19 with a mean of 1.28 comparing favorably with the average of all the studies of 1.27. This study by Nagase et al. also shows that individual hairs from Asians can vary in ellipticity from nearly circular to highly elliptical.

Trotter and Dawson [133] and Trotter [131] measured ellipticity on 6,400 Caucasian hair fibers from 242 males and 398 females. This study is described in more detail in the next section of this Chapter. Statistical analysis indicated no difference in ellipticity between males and females. Ellipticity for these 6,400 hairs varied from 1.09 to 2.13 similar to the range found by Nagase et al. on the hair of Japanese females. Note that the ranges for these two studies are similar, but the means are different 1.36 for Caucasians versus 1.28 for the Japanese. Also, the ranges are larger than for the Africans because of the much larger number of hairs used in the Caucasian and Japanese studies. These distributions are obviously not Gaussian, but when 25 or more hairs are averaged the means are quite reliable. Also note that, the size and shape of hair fibers vary along the fiber length as described earlier. Some of these variations have been attributed by Orwin [142] to growth patterns and environmental effects.

9.7.3.4 Hair Fiber Ellipticity and Age Among Caucasians and Asians

Hair Fiber Ellipticity and Age Among Caucasians

To date, I have been able to find several studies of hair fiber ellipticity versus age [131, 133, 143]. Three of these papers are from the anthropological literature by Trotter and cited in the previous section. In Trotter's earliest paper [131], she took hair from 340 Caucasians (American whites) ages 0–79 and measured the major and minor axis diameters of hairs taken from the vertex and calculated both cross-sectional sizes and ellipticity. Ten hairs were used per subject.

Trotter and Dawson [133] also measured the major and minor axis of 10 hairs per subject from the vertex of 300 Caucasians (French Canadians), 122 males and 178 females age 1–89. If we combine the results of these two studies we have ellipticity measurements of 6,400 hairs from Caucasians. The results are summarized in Table 9.18 showing an average ellipticity of 1.36 for Caucasians with a range of 1.09–2.13 in the study on Americans. Trotter separated the data for the French Canadians into seven different age groups for males and females and eight different age groups for the American Caucasians allowing matched pairs statistical analysis testing for seven groups of the data showing no significant difference for the ellipticity between Caucasian males and females in both studies and an average ellipticity of 1.36 for Caucasians.

Hair Fiber Ellipticity for Caucasians from Infancy Through Childhood

Trotter and Duggins [143] ran another study among Caucasian children by having hair sent to them periodically at 1 year intervals starting with infants through puberty. This study was discontinued after 17 years because of drop-outs. These scientists started with 15 infants each at 1 month (50 hairs) and 7 months (50 hairs) and summed these two data points to represent 100 hairs at age 1 (closer to ½ year). Then they measured 100 hairs from each of these same 15 subjects at 2 years of age, with one additional child at age 2 and continued with these 16 children until age 7. At age 8 one dropped out, but at age 11 four other children dropped out until age 13

Table 9.18 Hair ellipticity for two groups of Caucasians [131, 133]

Group	No. subjects		Mean ellipticity		Ellipticity range	
	Males	Females	Males	Females	Males	Females
French Canadians	122	178	1.37	1.38		
American Caucasians	120	220	1.35	1.34	1.09–1.75	1.11–2.13
Total Caucasians	242	378	1.36	1.36	1.09–1.75	1.11–2.13
Matched pairs test[a]	Prob $< t = 0.28$		Prob $< t = 0.69$		1.31–1.43	1.27[b]–1.48

[a]Note, the mean ellipticities for males and females are exactly the same. The matched pairs groups (seven pairs or groups of the same ages) were not matched in terms of numbers of subjects
[b]Only eight subjects in this group

Table 9.19 Means for the effects of age on the hair index from approximately 1 month through age 10 for the same 14 Caucasian children

Age	Average index[a]	Maximum/minimum diameter (ellipticity)
1 month	79.42[b]	1.26
2 years	69.36	1.44
3 years	69.64	1.44
4 years	70.93	1.41
5 years	70.71	1.41
6 years	72.07	1.39
7 years	72.07	1.37
8 years	73.07	1.37
9 years	73.14	1.37
10 years	72.29	1.38
7 months	73.57	1.36

[a]The hair index is the ratio of the minimum diameter to the maximum diameter times 100. The ellipticity is the reciprocal of the index times 100

Data were evaluated by the Wilcoxon signed rank test for paired observations, and [b]indicates the values that are significantly different from all others. The lines indicate the values that are not significantly different from each other

when four more dropped out rendering the study suspect beyond 10 years of age. Their data up to 10 years of age are summarized in Table 9.19.

Not counting the 1 month and 7 month sampling, Trotter and Duggins had collected yearly data points measuring 100 hairs from each of 14 subjects from age "1" through age 10. Trotter and Duggins [143] commented on the small difference found between the males versus females. However, since only six males and eight females were in this study I concluded that the sample size is too small for a meaningful comparison.

I analyzed these data of Trotter and Duggins by not combining the 1 month and 7 month data and by not examining data beyond age 10. I used the Wilcoxon signed rank test for paired observations. The results are summarized in Table 9.19 and demonstrated that the largest change occurs after 1 month where the hair is more round in the earliest stage of infancy. The 1 month data is significantly different from all other ages including the 7 month measurement ($P < 0.0001$). It would also appear from diameters that another change occurs a few years later.

Hair Fiber Ellipticity Versus Age Among Asians

Another useful study on ellipticity versus age is at higher ages and is from a paper by Nagase et al. on Japanese hair [144]. The authors of this paper [144] measured ellipticity among 132 Japanese females. These scientists found no statistically significant effect for the variation of ellipticity with age from 10 to 70 years.

Regression analysis provided an average ellipticity of 1.28 with a significant p value, but an index of determination (r^2) of 0.0001 showing that the variation in ellipticity by age among Japanese females was very small (0.01%) or not meaningful.

This study on the hair of Japanese women shows no effect of age on hair fiber ellipticity between the ages of 10–70 while two studies on Caucasian males and females over a similar age range also showed no effects of age on scalp hair fiber ellipticity. I would speculate a similar effect for African hair, but not with a high level of confidence because of the very large hair fiber ellipticity among that geo-ethnic group.

9.7.3.5 Fiber Diameter, Cross-Sectional Area, Fine Coarse Hair and Age and Hair Growth

Infants' is Finest and Children's' Hair is Fine; for Females it is Coarsest (Largest Diameter) Near the Mid-Forties but Males' Hair is Coarsest in the Late Teens to Early Twenties

As described in Chap. 1, the mechanism for hair growth involves three stages: a growing period called anagen; a transition period, catagen and a resting period, telogen. At telogen, the "old" hair falls out and is replaced by a "new" hair fiber. The time-span of the growth period (anagen) determines how coarse and how long scalp hair fibers will become. The time-span of anagen is shortest for infants, longer for children and longest from puberty to young adulthood, see Table 9.20.

Trotter and Duggins [143] studied hair fiber cross-sectional areas from infancy through childhood on the same 14 Caucasian subjects that they studied ellipticity from 1 month through 10 years of age. Their cross-sectional area data along with fiber diameters (calculated assuming circularity) are summarized in Table 9.21.

The data of Table 9.21 were analyzed by the Wilcoxon signed-rank test for paired observations showing highly significant differences between the cross-sectional areas at 1 month, 7 months and 2 and 3 years from all other ages. Several of the other pairs were not significantly different as indicated by the connecting lines

Table 9.20 Hair growth period, fine coarse hair and hair length of Caucasians females

Hair type	Approximate Max. length (cm)	Approximate Diameter (μm)	Est. anagen (Yr)
Infant	~15	30 (N = 26)[a]	~0.5
Children (0–9)	~60	62 (N = 82)[b]	~4 yr
Adult (15–29)	~100	74 (N = 98)[b]	~6 yr
Adult (30–89)	–	70 (N = 75)[b]	~5 yr
Vellus	~0.1	~4	–

[a]Pecoraro V et al. [146], 26 full-term infants; hairs taken within 76 h of birth (13 males and 13 females)

[b]Calculated from Bogaty [145] and from Trotter and Dawson [131, 133]

Table 9.21 Cross-sectional area and calculated average diameters versus age for hair from Caucasian children from Trotter and Duggins [143]

Age	Cross-sectional area (μm^2)	Calculated average diameter (μm)
1 month	529[b]	31
7 months	957[b]	35
2 years	1,929[b]	50
3	2,357[b]	55
4	2,721	59
5	2,787	60
6	3,064	63
7	3,193	64
8	3,271	65
9	3,407	66
10	3,457	66

[a]Diameters calculated assuming circularity
[b]Significantly different from all other values. Lines indicate those values that are not significantly different from each other by the matched pairs test

in this table. Clearly, the cross-sectional areas are smallest at 1 month. The cross-sectional areas and therefore average diameters are also smaller at 7 months, 2 years and 3 years compared with all other values except 1 month. Three to four times the percentage change in cross-sectional area occurs between 1 and 7 months and 7 months and 2 years compared to the total change that occurs between 4 and 7 years of age. These dimensional changes in the hair fiber correspond reasonably well with the generalized description by Furdon and Clark [147] that the fine hair of infants tends to be lost by about the sixth or seventh month and is replaced by a coarser hair that grows longer. This hair then is replaced by an even coarser hair at about 2–3 years of age that grows even longer.

Hair Fiber Diameter Versus Age for Males and Females

The study by Otsuka and Nemoto [134] on the hair of Japanese males (1,177) and females (7,580) between the ages of 10 and 60 shows a larger and earlier decrease in hair fiber diameter for men than for women; see Tables 9.22 and 9.23.

For Japanese males, the study by Otsuka and Nemoto shows that scalp hair fiber diameter increases to a maximum to the late teenage years and then it decreases relatively rapidly with increasing age, see Fig. 1.10. These data suggest that for Japanese women, scalp hair diameter increases to a maximum near the age of 40 and decreases thereafter.

Similar effects (a peak in diameter during the teenage years for males followed by a gradual decline after that and an increase in diameter for women during the teens to the 40s when a decline begins) can be seen in a study by Trotter and Dawson [133] for hair of French Canadians (see Table 9.23). Trotter and Dawson noted this effect was not statistically significant by comparing subgroups of males

Table 9.22 Hair fiber diameters versus age for Japanese men and women [134][a]

Predicted diameter(μm)		
Age	Men	Women
15	84	79
20	84	81
25	83	82
30	81	82
35	79	82
40	76	82
45	72	80
50	68	78
55	63	75

[a]Data points were estimated from a graph in this paper [134] and prediction equations calculated. Data points for diameters of the table are from the prediction equations and all were within ±1% of the graph data points rounded off to the nearest micrometer. Prediction equations were, for men $Y = 95.58 - 0.484\ X - 0.01279(X - 32.75)^2$; for women $Y = 84.11 - 0.0483\ X - 0.01387\ (X - 33.7)^2$ where Y = predicted diameter and X = age

Table 9.23 Scalp hair fiber diameter (in μm) and age for males and females

Approximate ages					
	10–14	15–19	20–29	30–49	50 plus
[a]Males Japanese	84	86	83	78	63
[b]Males French Canadians	68	74	73	71	64

Instantaneous rates of change of scalp hair diameter (OFD) for Caucasian females by age £

	Instantaneous rates of change of diameter in μm/year	
Age	Average instantaneous rate[a]	Mean diameter (μm)[b]
25	0.45	63.94
30	0.33	65.90
35	0.22	67.27
40	0.097	68.06
45	−0.021	68.25
50	−0.14	67.86
55	−0.26	66.86
60	−0.38	65.27

[a]Average of instantaneous rates from regression models
[b]Calculated mean diameter values from model for OFD
£ Robbins and Dawson et al. [148]; maximum for female Caucasians between ages 43 and 46

versus females. However, the study of Trotter and Dawson involved only 136 females and 82 males compared to 18,262 females and 1,177 males in the Japanese study.

The work of Courtois et al. [124] comparing hair fiber diameters on the same male subjects over a period of several years provides support for a decrease in hair diameter of male Caucasians with age between the ages of 25 and 49. Courtois et al. [124] studied 10 Caucasian adult male subjects (starting at ages 25 up to 49 years of age) by making observations periodically over 14 years. These scientists demonstrated a reduction in the duration of the growth period (anagen) coupled with a decrease in the diameter of hair shafts with increasing age. In addition, the time interval separating the loss of a hair in telogen and the appearance of a replacement hair in anagen also increased.

Therefore, this study by Courtois et al. [124] on Caucasian adult males demonstrated that hairs on the same male Caucasians after puberty become finer over the years confirming the conclusions of Otsuka and Nemoto [134] on age and fiber diameter on different Japanese males. This study by Courtois et al. on adult Caucasian males also confirms the conclusions on the effects of age on the diameter of scalp hair of male Caucasians from the French Canadian data of Trotter and Dawson.

A very large study by Robbins and Dawson et al. [148] measured mean hair fiber diameters from 250 to 400 hair fibers from each of two sites one on the left and one on the right parietal region on more than 1,000 female Caucasians from age 18 to 66. In this study both an Optical Fiber Diameter (OFD) system and an Image Analysis system were used for diameter measurement; therefore, these data were not included in Table 9.14. However, data comparing the OFD method with laser, microscopic and linear density methods on the same 39 hair samples demonstrated 77.31 μm for the OFD and 75.57 μm for the laser (no significant difference), 71.34 μm for the linear density and 66.7 μm for the microscopic method with both of the latter methods providing significantly different diameters from the OFD method.

The OFD and the IA data from this large study of female Caucasians were regressed against age providing a curvilinear relationship, see Fig. 9.19. The maximum mean fiber diameter occurred between 43 and 46 years of age (by both diameter measurements) and is likely linked to the peri-menopause. The quadratic equation for the OFD method provided a $p < 0.0001$, $r^2 = 0.0257$ and a root mean square error of 9.380 with a maximum diameter at age 43. A cubic equation provided a $p < 0.0001$, $r^2 = 0.0282$ and the root mean square error was 9.370 and a maximum diameter at age 46, see Fig. 9.19. Data from the quadratic model along with instantaneous rates of diameter change with age are summarized in Table 9.23.

The data from Table 9.23 shows that hair fiber diameter in the parietal region of female Caucasians increased from about age 18 until about 43–46 whereupon it peaked and then decreased with increasing age. This effect contrasts with data for males [131, 133, 134] where the maximum for mean fiber diameter peaks in the late teens to early twenties, see Tables 9.22 and 9.23.

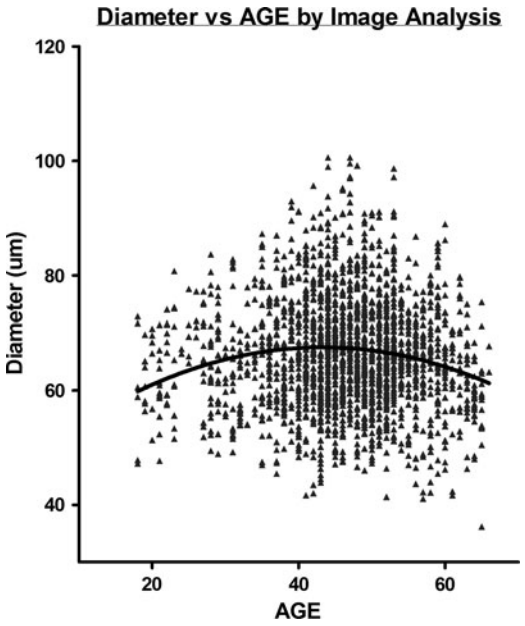

Fig. 9.19 Hair fiber diameter for Caucasian females by an image analysis method from Robbins and Dawson et al. [148]

Data for scalp hair diameter of Japanese females has been shown to occur somewhere around the age of 40 [134] and the median menopausal age occurs at about 50–51 for women of most industrialized countries including Japan. Therefore, it is likely that menopausal status has a similar effect on scalp hair diameter of women of most industrialized countries and that estrogens are somehow involved in hair fiber diameter. Therefore the mean fiber diameter for hair from Japanese women may actually be a little higher than found in the study by Otsuka and Nemoto and closer to the age of 43–46 as shown for Caucasian women by Robbins and Dawson et al.

The quadratic model for the subjects in the Robbins and Dawson et al. study suggests that the instantaneous rates of change of diameter (Table 9.23) or the speed of hair diameter change actually decreased at a constant rate of −0.0236 μM/year (2nd derivative of the quadratic model). Even though the actual diameter increased from age 20 to about 45 the rate and amount of diameter increase actually decreased and it continued to decrease at this constant rate to about age 45 whereupon the diameter began to decrease and this process continued with advancing age.

The Effect of Scalp Site on Hair Fiber Diameter

Mirmirani and Dawson et al. [149] demonstrated that mean fiber diameters for female Caucasians are significantly higher in pre- versus post-menopausal women for the frontal but not the occipital site. The larger study by Robbins and Dawson et al. [148] shows that the parietal region follows a similar pattern to the frontal site. The

maximum mean fiber diameter in the parietal region occurred in the vicinity of the peri-menopause which is characterized by irregular periods or cessation of periods for less than 12 months. These studies collectively suggested that menopausal status has a major impact on scalp hair fiber diameter for the frontal and parietal regions but not the occipital site. This study also suggests that more studies on different scalp sites are necessary to fully understand the properties of human scalp hair.

The follicle is the sac that each mammalian hair fiber grows in. In sheep, fine-wool breeds tend to have follicles of narrower diameters whereas longer follicles correlate with longer wool fibers as shown by Orwin [152]. We would expect similar trends to exist in human hair. Furthermore, Lindelof et al. [150] provided evidence that the size and shape of the human hair follicle tends to correlate with the hair fiber shape. However, there is strong evidence that hair fiber composition and the distribution and orientation of different proteins in the cortex provide the major contribution to the hair fiber shape (see Chap. 1 for a more complete discussion of this subject).

Why Hair Fiber Diameter of Males Versus Females Provides Inconsistent Results

Steggarda and Seibert [129] examined scalp hair fibers from six different racial groups and claimed significant differences by sex. However, these scientists examined hair fibers from only five males and five females for each group measuring 70–100 hairs from each person.

The confusion in the scientific literature about the diameter of hair of males versus females can be explained by examining the studies of Otsuka and Nemoto [134], Robbins and Dawson [148] and the work of Trotter and H.L. Dawson as summarized in the preceding section. These studies all show that hair fiber diameter for females increases until about 40–46 years of age, however the work of Otsuka and Nemoto and Trotter and Dawson and Courtois all show that the diameter of scalp hair of males peaks much earlier, somewhere near the age of 20. Therefore, diameter comparison of the scalp hair of males versus females is most likely very dependent on the sampling ages. If additional differences exist between the scalp hair of males and females due to geo-racial effects (between Asians and Caucasians) these will only be evident after larger scale comparative studies are conducted.

The largest difference in the diameter between hair of males and females most likely occurs at middle age (near ages 35–46), where the diameter of the hair of females is near a maximum and the diameter of the hair of males had been decreasing for about two decades. This difference most likely will become smaller as we move to younger ages from middle age to the teenage years and should either become equal or cross over near ages 15–20.

Fine Hairs do not Grow as Long in Length as Coarse Hairs

Infants' hair generally does not exceed 15 cm length and it is very fine. Pecoraro et al. [146] examined the hair of 26 new born infants within 76 h of birth. These scientists found that the average diameter was 30 μm and estimated the anagen period to be only a few weeks. Children's' hair prior to puberty usually does not exceed 60 cm long and it is coarser than infant's hair as shown by Bogaty [145]. But, adult hair has the capacity to grow even longer and is even coarser. With advancing age, hair fibers become finer [131, 133, 134, 148] and will not grow as coarse [124, 134] or as long as in prior adulthood. Courtois et al. [124] demonstrated for male Caucasians that with increasing age beyond puberty, anagen becomes shorter. Saitoh et al. [151] examined the hair of one Japanese male at 60 years of age. Saitoh et al. found the average anagen for hair fibers growing on the vertex of the scalp was 23 weeks and the range was 17–94 weeks for "coarse" hair. These same scientists [151] found longer anagen time spans for two other subjects 21 and 30 years of age, but the time spans for anagen exceeded the time allocated for writing the paper so additional data was not available.

Because of the relationship of the time-span of anagen to hair fullness on the scalp and to longer and coarser hairs, anagen to telogen ratios have been used to measure either hair growth or hair loss. The evidence shows that coarse hairs on the same person become finer with advancing age [124] confirming the conclusions of Otsuka and Nemoto [134] on age and fiber diameter on different persons. Furthermore, the growth period and hair length (if never cut) also become shorter. These facts suggest that neighboring hairs on the same scalp that are finer should also not grow to as long a length as coarser hairs (never cut). Furthermore, fine versus coarse hairs among different persons will likely not grow as long in length and they will have a shorter anagen time span.

Hair Fiber Diameter Varies by a Factor of About 2 on Each Scalp

Most of the work in the scientific literature is on scalp hair from the vertex or the crown area of the scalp, although hair from other areas of the scalp is sometimes used [149]. Garn in his PhD thesis at Harvard University in 1948 was one of the first to claim that scalp hair is finest at the temples and most coarse at the lower sideburns on "normal" scalps. "Normal" scalp usually means pre-alopecia or before the phenomenon of balding begins. The lower sideburns are actually beard hair which is coarser than scalp hair of the vertex. Tolgyesi et al. [152] demonstrated that beard hair also contains a higher amount or higher percentage of hairs with medulla. Beard hair is also more elliptical and has more irregular cross-sectional shapes than scalp hair. Beard hair also has lower disulfide content (cross-link density) than human scalp hair [152].

For adult Caucasian individuals, the average diameter (from the vertex or crown areas) usually ranges from about 46 to about 94 micrometers. Scalp hair diameter shows large differences among neighboring hairs on the same head, ranging from a

factor of less than 1.4 to more than 2.0 on adult Caucasian women [112]. Garn is essentially in agreement with Yin et al. [112] on these ranges on an individual scalp, claiming as early as 1948 that the average diameter of neighboring hairs on the same scalp may vary by more than a factor of 2. Hair on different regions of the scalp grows at different rates as described in Chap. 1. DeBerker et al. [153] have shown that on "normal" scalps, hair grows slowest on the temples (0.39 mm/day for males ~14 cm/yr) and faster on the vertex (0.44 mm/day for males ~16 cm/yr) where it grows coarser.

Fine Hair Tends to be Lighter in Color than Coarse Hair

The extreme case supporting this conclusion is that vellus hair, the finest of all hairs does not contain pigment, whereas most permanent hairs the coarsest of scalp hairs generally contain pigment. Caucasian hair on average is finer than Asian or African hair and on average it is lighter in color. Schwan-Jonczyk [154] demonstrated that the size of the pigment granules in scalp hair is larger in Asian and African hair than in Caucasian hair. Fitzpatrick et al. [155] described that the hair of Africans tends to be black and that the pigment granules of the hair of those of African descent tend to be larger than those of dark European hair. Schwan-Jonczyk [154] also determined that the pigment granules from dark European hair are on average larger than those of blonde and red hair.

In addition to pigment size, the main pigment of darker hair is eumelanin, whereas pheomelanin is the primary pigment of most red and some blonde hairs. There are undoubtedly exceptions to this conclusion that fine hair tends to be lighter in color than coarse hair, because hair color is determined by several variables including the type of melanin pigment, the size of the pigment granules and the density (frequency) of the pigment granules that are dispersed throughout the cortex of human scalp hairs, however there are several other references supporting this conclusion and some of these are described below, also see Chap. 5 for additional details.

Pecoraro et al. [146] examined hair from 26 infants within 76 h of birth considering hairs from 13 males and 13 females. These scientists found that the mean coarseness of dark hairs from dark complexioned newborns was 37 μm while the average diameter for light colored hairs from light complexioned newborns was 22 μm.

Trotter and Dawson [131, 133] examined hair of children and adult Caucasians (French Canadians and Americans). They concluded that coarse hair tends to be darker than fine hair [131, 133]. In addition, Bogaty [145] concluded from his review of the anthropological literature that Caucasian children's hair is on average finer, rounder, less frequently medullated and lighter in color than adult's hair, see Table 9.24.

Table 9.24 Caucasian children's hair is finer and lighter than adult's (N = 310)[a]

Ages	Diameter (μ)	% brown-black	% blond-dark blond	% light blond
0–4	58	35	50	15
5–9	66	75	22	3
10–14	69	96	4	0
15–19	74	98	2	0
20–29	73	98	2	0
30+	70	97	3	0

[a]Data from anthropological study of French Canadian hair by Trotter and Dawson [133]

Is Gray Hair Coarser than Highly Pigmented Hairs on the Same Scalp?

Whether gray hair is coarser than highly pigmented hairs on the same head is still in question because of mixed results. This subject is covered in detail in Chap. 5 in the section entitled, *Hair Pigment Structure and Chemical Oxidation*. See these [156, 157] and other relevant references in Chap. 5.

Cross-Sectional Size and Hair Fiber Curvature

Porter et al. [47] found a significant negative correlation between hair fiber curvature and cross-sectional area ($R^2 = 0.98$) from 12,050 African type hair fibers that varied from curl class IV to VIII, see Table 9.25. Therefore, 98% of the variation in cross-sectional area of this type of hair over this curvature range can be explained by hair fiber curvature and the cross-sectional area decreased with increasing fiber curvature over this curvature range.

Even though we were unable to find direct data on curl type versus cross-sectional area for Asian or Caucasian hair, the data of Table 9.25 shows this same directional trend on averages for cross sectional area and curvature for these three hair types. For example, the average cross-sectional area for Asian hair is highest and that for African hair is lowest with Caucasian hair in the middle. While the inverse holds for Curl Type. It will be interesting to see if this same trend exists within these populations (Asians and Caucasians), because if it does then hair fiber

Table 9.25 Cross-sectional areas and curvature for average Asian, African and Caucasian hair

Hair type	Ave D	Max D/Min D	Cross-sectional area	Ave. curl type
Asian	82	93.4/72.7	5,333	II [158, 159]
Caucasian	70	82.8/60	3,902	II, III [158, 159]
African	72	93.6/55.8	4,104	IV to VIII [158, 159]

Diameter values in μm and area in μm^2 (average D is from Table 9.14)
All other values calculated from these equations via iteration
Elliptical Ratio = Max D/Min D

$$\text{Ave D} = \sqrt{\text{Dmax} \times \text{D min}}$$

$$\text{Cross-sectionalarea} = \pi\ \text{Rmax} \times \text{Rmin}\ (\text{R} = \text{radius})$$

curvature could be calculated from cross-sectional area data provided a suitable model equation could be developed.

Hair fiber diameter correlates positively with cross-sectional area. Otsuka and Nemoto [134] have shown that hair fiber diameter of Japanese females from ages 40 and up decreases with age. Furthermore, Nagase [93] determined that hair fiber curvature of the hair of Japanese females ages 10–70 increases with age. Therefore, we can conclude for Japanese females ages 40 and higher hair fiber curvature correlates negatively with diameter and cross-sectional area of hair.

9.7.4 Effects of Fiber Cross-Sectional Shape on Properties and Reactivity

The previous section shows how the fiber cross-sectional shape can vary between and within different geo-racial groups and Figs. 9.20–9.25 illustrates some of the shape variation of human hair. As indicated, hair fiber cross-sectional shape varies

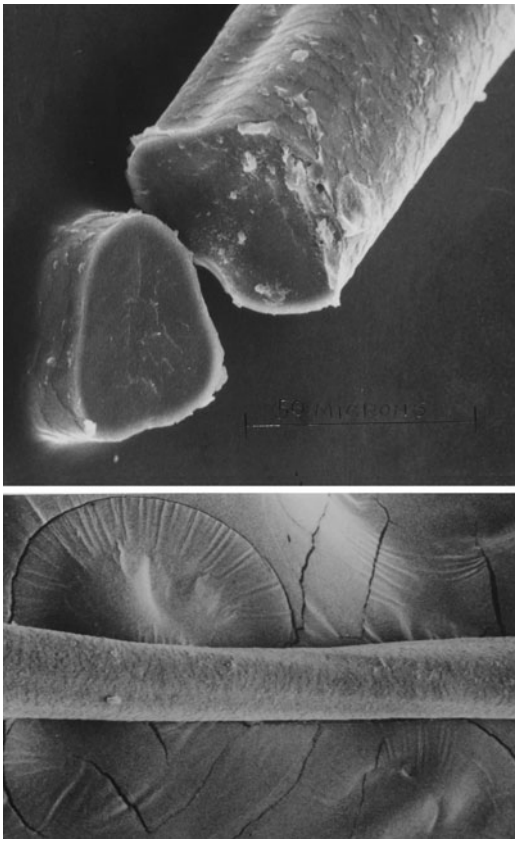

Fig. 9.20 Caucasian hair fiber with a slight twist (*bottom*) and flattened areas on the surface (*top*). Another common non-circular shape of Caucasian hair

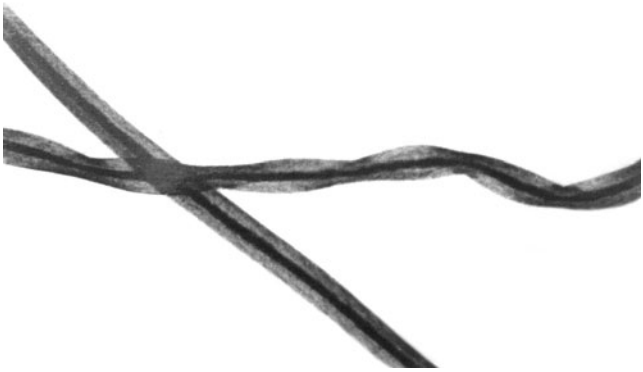

Fig. 9.21 African American hair fiber with multiple twists. Light micrograph kindly provided by John T. Wilson

Fig. 9.22 An African American hair fiber illustrating a fiber twist at higher magnification than for Fig. 9.21. Light micrograph kindly provided by John T. Wilson

within each geo-racial group and even on a single person's head. Even though we talk about the hair of Caucasians as representing relatively circular hair fibers, Figs. 9.20 and 9.23–9.25 show the "normal" variation that encompasses non-circular cross-sectional shapes that can be found on Caucasian scalp hair.

Indented areas are frequently observed (Fig. 9.20). Twists in human hair fibers are not un-common especially in African type hair (Figs. 9.21 and 9.22).

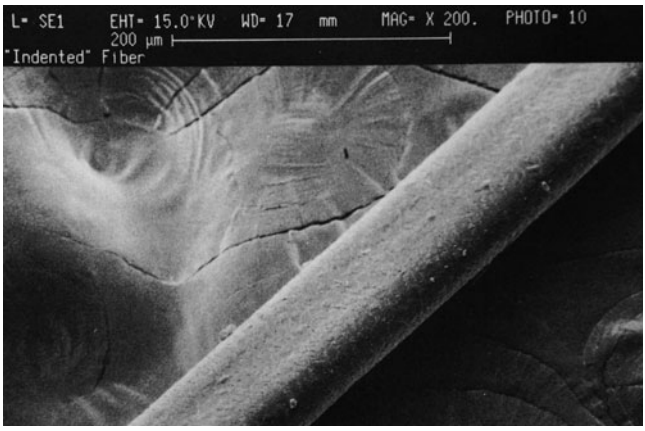

Fig. 9.23 A Caucasian hair fiber with a large indented area on its surface. Note the irregular shape on the rest of the hair created by this indent

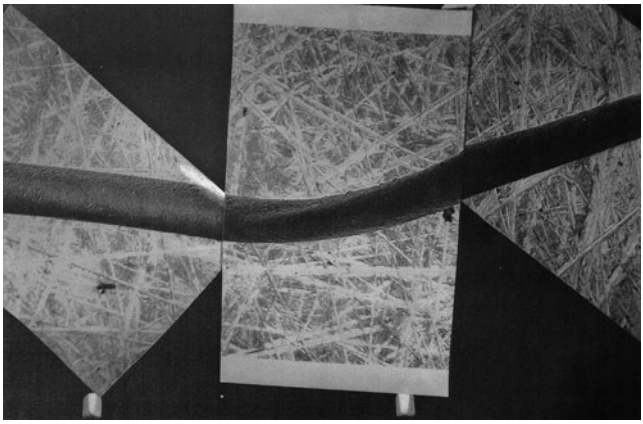

Fig. 9.24 An electron micrograph illustrating a common twist in a curl of a Caucasian hair fiber

Figures 9.20 and 9.24 illustrate twists in Caucasian hair and Figs. 9.21 and 9.22 showing more extensive twists in African American hair. Flat spots and high spots are also common (Figs. 9.23–9.25) in hair of all origins. Widely varying diameters occur in fibers from the same scalp and even on the same hair fiber. As indicated, a rule of thumb is that hair fiber diameter on the same scalp varies by about a factor of two [112].

These different fiber shapes affect not only the physical properties of the fiber such as fiber breakage and abrasion resistance, but, fiber shape also affects the physico-chemical reactivity of the fiber. Figure 9.25 shows an electron micrograph of an irregularly shaped hair fiber from the scalp of a Caucasian female. This fiber contains flat and high spots that form ridges along the axis of the

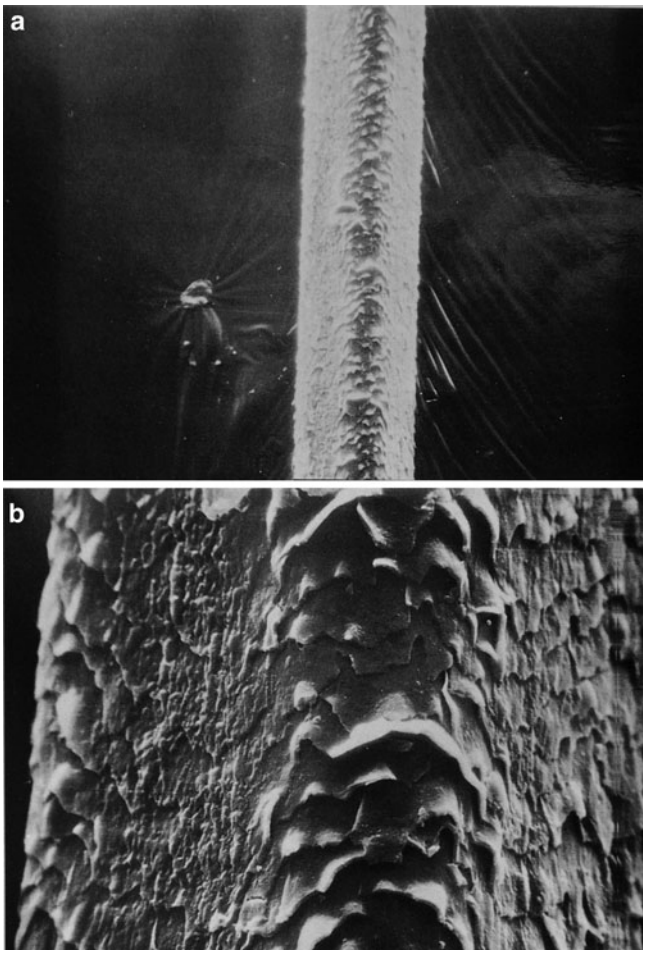

Fig. 9.25 Scale lifting on a highly irregular shaped hair fiber surface. Note the greater lifting on the fiber "high spot" where the scales are most severely bent

fiber. This hair fiber had previously been permanent waved and dyed on the scalp and then treated in the laboratory with alternating treatments of triethanolammonium lauryl sulfate and stearalkonium chloride. This type of treatment raises scales on fibers that are damaged in the cuticle cell membrane complex or the endocuticle.

The scale lifting that resulted occurred more on the high spots along the ridges of the fiber than on the flat areas. This effect in scale lifting not only represents a difference in reactivity along the fiber cross-section, it makes the scales on the ridges more susceptible to fragmentation and removal and subsequently makes these high spots more susceptible to further penetration and damage by chemical treatments and rubbing actions.

This fiber shape induced reactivity difference is only one example of the variation in reactivity on hair fibers caused by fiber shape variation. Undoubtedly many of the experimental variations that we observe in hair science that are difficult to explain may be caused by fiber shape variations and oftentimes they go unexplained.

9.7.5 Scale Type of Mammalian Hair is Related to Hair Fiber Diameter

A series of papers were written in the 1920s by Hausman [160] on structural features of the hair of mammals. Hausman classified cuticle scales of different mammals on the basis of their size and shape into two general kinds that he called imbricate and coronal, see Fig. 9.26. Hausman then divided the imbricate type scales into five different kinds and the coronal scales into three different kinds, see Fig. 9.26. Human scalp hairs fit into the flattened imbricate classification of Hausman. Hausman [160] defined the scale index as the scale interval (free proximo-distal diameter) of a cuticle scale (F) in Fig. 9.26 divided by the shaft diameter or F/D = scale index. After examining 190 samples of dorsal under-hair of many species of mammals, Hausman concluded that the scale index is related more to the diameter of the scales than to the scale type classes that the species have been assigned to, thus the scale index is inversely related to the diameter of the hair shaft.

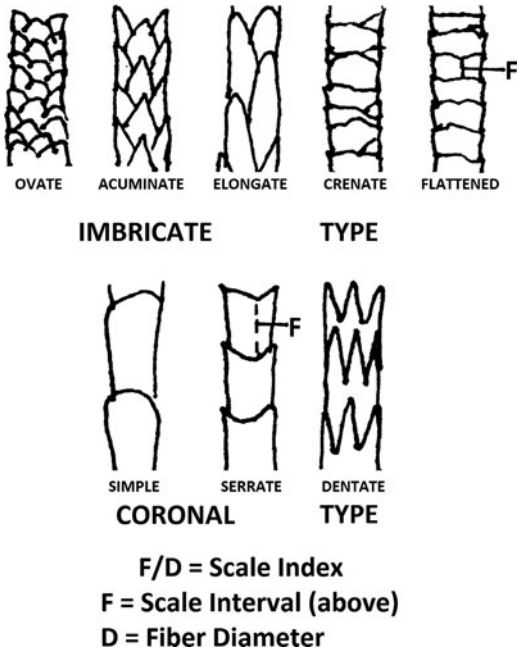

Fig. 9.26 The scale index and different scale shapes of mammalian hair fibers (adapted from Hausman [160])

Hausman did not provide a statistical model for this relationship. Therefore, I examined his graph of Scale Index versus fiber diameter for different mammalian species. From that graph, I estimated the Scale Index versus fiber diameter from 24 data points for different mammals over the range of 7–99 μm and using JMP statistical software calculated a quadratic model as the best fit with an R^2 of 0.916 and a p value of < 0.0001.

This equation $\{Y = 0.0382–0.01333\ X + 0.000209\ (X\text{-}48.0385)^2\}$ where Y = the predicted value of the scale index and X = fiber diameter provided predicted values for the scale index versus diameter as summarized in Table 9.26 The predicted data of this table show that the scale index is inversely related to the fiber diameter and this relationship is strong. An interesting observation is that Hausman did this work nearly 90 years ago and it is still very useful.

Wynkoop [161] examined the form of cuticle scales and the extent of medulla (described in Chap. 1) with respect to age. However, Wynkoop used too few subjects' times hairs. For example, other than age group 0–9 and 20–29, she used 3 hairs from only 1 to 9 persons per group. However, Wynkoop did show a better fit of scale index and extent of medulla with fiber diameter than with age. From what we currently know about fiber diameter, scale interval and extent of medulla, large variations are inherent in data of these variables. Therefore,

Table 9.26 Scale index versus hair fiber diameter for mammalian hair fibers [160]

Estimated scale index	Diameter	Predicted scale indices
1.48	7	1.31
1.3	9	1.22
1.02	11	1.13
1.1	12	1.08
0.7	15	0.96
0.88	18	0.86
0.68	20	0.79
0.7	24	0.96
0.52	26	0.62
0.78	27	0.60
0.4	34	0.45
0.5	36	0.42
0.48	38	0.39
0.38	42	0.34
0.26	50	0.27
0.22	60	0.22
0.16	70	0.20
0.14	74	0.19
0.16	76	0.18
0.20	78	0.18
0.18	83	0.16
0.07	93	0.09
0.06	96	0.06
0.06	99	0.03

I conclude that if Wynkoop would have used more hairs and more subjects for each age group, she would likely have shown a relationship of both scale index and age and the extent of medulla with age. For example since children's hair is finer than adults hair there should be more medulla in adult's hair than children's hair, see Chap. 1 in the section entitled *Medulla* for details on the medulla and fiber diameter.

Takahashi et al. [162] examined the scale interval for a large number of Asian and Caucasian scalp hair fibers. The total number of subjects was 89 Japanese and 214 Chinese for Asian hair and 160 Germans and 50 Americans for Caucasian hair. Two hundred and eighty two hairs from these Caucasian females and 200 hairs from the Asians were measured at more than 300 points on each hair fiber for the scale interval which was found to be 6.61 $\pm$ 0.52 μm for the Asian hair and 6.98 $\pm$ 0.60 μm for the Caucasian hair. This difference is significant beyond the 0.001 level. Using the average diameters for Asians and Caucasians from Table 9.14, I calculated the scale indices for these two groups to be 0.103 for the Caucasians and 0.0796 for the Asians hair. These values are reasonably close to the predicted values of 0.115 and 0.087 from the quadratic prediction equation for the data extracted from Hausman's graph on different mammalian species. See the section in Chap. 1 entitled *The Cuticle*.

The question now is what is the effect of the scale interval (F in Fig. 9.26) on hair properties? My conclusion is that since the scale index (F/D) is strongly correlated with hair fiber diameter then the scale interval F is also. So, if we normalize the data to fiber diameter the effects will largely be compensated for in our calculations. Furthermore, cuticle scale thickness (thickness of each cuticle cell times the number of cuticle layers) both of which Takahashi et al. [162] demonstrated to be larger in Asian versus Caucasian hair will play a stronger role than the scale interval or scale index in fiber reactivity. Takahashi et al. in this same paper determined that wet cuticle fragmentation is different in Japanese versus Caucasian hair. Therefore, the cuticle composition including the ratio of exocuticle (A-layer plus exocuticle) to endocuticle will play a larger role in cuticle damage than the scale interval or the scale index. I also conclude that the primary changes versus age of these parameters will occur in infants, versus children's versus adults' hair with possibly the elderly being different from younger adults. However, none of these effects have been examined to date.

9.8 Hair Fiber Curvature

9.8.1 Factors Related to the Origin of Fiber Shape

Not considering permanent waving or straightening, the longitudinal fiber shape (curvature) is genetically determined (see Figs. 9.27 and 9.28). Curvature is related to the degree of coiling including natural crimps and bends of hair fibers and is the

Fig. 9.27 Hair of different fiber curvatures illustrating how hair assembly volume increases with curvature by the Robbins–Reich method

Fig. 9.28 Hair of different fiber curvatures by the Segmentation Tree Analysis Method (STAM) illustrating curvatures from level I to VII. I could not find hair of level VIII for this illustration

most important fiber characteristic involved in styling, combing, and other aspects of hair assembly behavior. Permanent waves and hair relaxers function primarily by changing fiber curvature to produce either a curlier or a straighter hair. Figure 9.27 depicts hair fiber curvature by the Robbins–Reich system and Fig. 9.28 by the STAM. When curvature is low, the hair is relatively straight as in tresses with ratings of 0, 2 and 4 in Fig. 9.27 and STAM I and II in Fig. 9.28. When hair is relatively straight, friction and stiffness play a very important role in hair assembly behavior. However, when the hair is very curly as in tress 16 by Robbins–Reich or IV by STAM or even curlier, then fiber curvature has the ability to dominate other fiber properties and control hair effects.

The Robbins–Reich method for determining hair fiber curvature works well for curl classes I through IV (Fig. 9.28), but does not distinguish as well as STAM for higher curvatures. Furthermore, since the STAM curvature method has been applied to so many subjects (more than 2,400) in so many different countries and it can be applied to curl types I to VI from curl radius or curl diameter data or even calculated from hair fiber ellipticity; for these reasons this author recommends the STAM method for hair fiber curvature over his own method.

The dominant feature relevant to the origin of hair fiber shape is the distribution of different types of cortical cells in the fiber. In general, hairs that are straight contain a distribution of cortical cells that may be pictured as concentric circles. That is they are symmetrically arranged about a common axis in the center of the fiber. On the other hand, curly hairs contain different types of cortical cells on the inside of the curl relative to the outside of a curl. Therefore, the cortical cells of curly hairs tend to be distributed more in a bilateral type arrangement. For a more complete discussion of hair fiber shape including a review of the current status of the origin of hair fiber shape see the section in Chap. 1 entitled *The Origin of Hair Fiber Curvature*.

9.8.2 A Historical View of Approaches to Measure Hair Curvature

Many attempts have been made to classify the longitudinal shape or the curvature of human hair fibers both in the anthropological and cosmetic fields of hair science. In a review paper, Trotter [163] described the history of curvature classification wherein she indicated that in the early nineteenth century, there were two qualitative distinctions for human hair, straight-wavy hair and wooly or tufted hair. The next meaningful step in the classification of hair curvature occurred in the mid to late nineteenth century and involved combinations of curvature and cross-sectional shape characteristics. Then in 1900, Deniker [164] provided four semi-quantitative classes for curvature for physical anthropology:

Straight and smooth hair
Wavy hair: a long curve from one end to the other
Frizzy hair: hair rolled spirally with rings 1 cm or more in diameter
Wooly hair: spiral curves from 1 to 9 mm in diameter

Martin in 1928 [165] published his 3 major curvature classes with sub-groups:

Smooth: straight, smooth, shallow wave subgroups
Wavy: wide waves, narrow waves, curly subgroups
Kinky: frizzy, loose kinks, tight kinks, tight spirals subgroups

Another important step was to provide more quantitative classifications or definitions for the longitudinal shape of hairs. Hardy [48] defined several longitudinal shape characteristics and measured these for seven different populations including the following:

Kink: "a sudden constriction and twisting of the hair shaft producing an obvious discontinuity in curvature".
Curl radius or radius of Curvature: compare each curve of a hair to curves of a transparent template consisting of circles of known radius.
Average Curvature: is "the inverse of the average radius of curvature".
Ratio of maximum to minimum curvature: Ratio of the "highest to lowest" radius of curvature of a hair fiber.
Crimp: (Hardy adopted the definition of the wool industry) "number of times the direction of curvature changes per unit length".
"Ratio of natural to straight length": the effect of curling on the hair fiber length.

Others have used some of Hardy's definitions or minor modifications to approximate or assess hair fiber curvature. For example, Nagase et al. [93] and Kajiura et al. [166] used the curl radius. Robbins and Crawford [167] used the inverse of the ratio of maximum to minimum length. Porter et al. [47] used curl diameter and De La Mettrie et al. [158] and Loussouarn [159] combined three parameters used separately by others including curl diameter, the ratio of maximum to minimum length [3, 48, 167] and the number of wave crests for a given length [3]. Robbins and Reich [3] described another approach based on the number of wave crests divided by the ratio of the minimum to maximum length, see Fig. 9.27. But, to date none of these methods have received wide acceptance outside of their own laboratories.

The STAM described first by De La Mettrie et al. [158] classified the curvature of hair from 1,442 subjects, see Fig. 9.28. Subsequently, Loussouarn et al. [159] published data with measurements and curvature classification on hair from an additional 1,007 subjects. A third paper from this same laboratory by Porter et al. [47] used the STAM to examine the behavior of African type hair as a function of curvature and provided minor adjustments to the original parameters for classification.

Using data from several different researchers and technical papers [48, 129, 166, 168] where either curl radius or curl diameter are provided, one can show that this measurement permits meaningful classifications, over the first five curl groups. Furthermore, ellipticity [47] may be used to calculate Curl type classes between IV and VIII when STAM curl typing has not been done. Such a method for the entire curl range is described in the next section of this Chapter, entitled *Curvature by the STAM method can be approximated by Calculation from Ellipticity*.

The STAM method consists of measuring three parameters after the 6 cm hair fibers are washed in dilute detergent rinsed with water and allowed to dry to their natural curvature for at least 5 min:

The smallest curl diameter is then measured for each fiber = CD
The ratio of the straight length 6 cm to the curled length is then taken = $L_6//L_C$
The number of wave crests are counted on a 5 cm fiber when it is held at 4 cm = W

Curvature is then classified by the following criteria:

$$\text{Curl Type I} = \text{CD} > 10.8 \text{ cm}$$

$$\text{Curl Type II} = \text{CD between } 5.7 \text{ and } 10.8 \text{ cm}$$

$$\text{Curl Type III} = \text{CD between } 3.1 \text{ and } 5.7 \text{ cm}$$

$$\text{Curl Type IV} = \text{CD between } 1.2 \text{ and } 3.1 \text{ cm}$$

$$\text{Curl Type V} = \text{CD} < 1.2 \text{ cm and } L_6/L_C < 5.9 \text{ and W} < \text{or} = 3 \text{ waves}$$

$$\text{Curl Type VI} = \text{CD} < 1.2 \text{ cm and } L_6/L_C < 5.9 \text{ and W} = \text{or} > 4 \text{ waves}$$

$$\text{Curl Type VII} = \text{CD} < 1.2 \text{ cm and } L_6/L_C > 5.9 \text{ and W} = \text{or} > 5 \text{ waves}$$

$$\text{Curl Type VIII} = \text{CD} < 1.2 \text{ cm and } L_6/L_C > 5.9 \text{ and W} = \text{or} > 6 \text{ waves}$$

Curl types I through IV are classified by curl diameter alone. The other measurements are used to distinguish between Curl types V through VIII.

9.8.3 *Curvature by the STAM Method can be Approximated from Ellipticity*

Ellipticity has been shown to increase with fiber curvature in separate studies with large numbers of hair fibers on hair of widely differing curvatures, one study on Japanese hair by Nagase et al. [93] on more than 8,900 hair fibers (small effect) and another study on African type hair by Porter et al. [47] on more than 12,000 hair fibers (larger effect). Since these two ranges of ellipticity and curvature cover the entire scale of curvatures and ellipticity for human scalp hair, this relationship should exist for all geo-racial hair including Caucasian. A regression equation was calculated by taking a total of 9 data points, 3 directly from the graph of Nagase et al. [93] and 5 from the prediction equation from Porter et al. [47]. One further assumption was that an ideal ellipticity of 1 occurs at an ideal Curl type of 1 for STAM Curvature [47]. The relationship is best described by this cubic equation of the natural logarithm of Curvature versus Ellipticity (E):

$$\ln \text{Curl type} = -1.8087 + 1.9765\ \text{E} + 4.0319(\text{E} - 1.474)^2 + 10.039(\text{E} - 1.474)^3$$

$$\text{The } R^2 = 0.9993;\ p < 0.0001 \text{ and Root Mean Square Error} = 0.02351$$

Table 9.27 Calculation of STAM curl type from ellipticity

Type of hair	Ave. curl type[a]	Calc. curl type[b]	Ave. ellipticity
£	1.0	1.0	1.0
€	2.3	2.43	1.34
€	2.6	2.9	1.45
€	4	4.15	1.596
¥	5	4.7	1.63
¥	6	5.54	1.668
¥	7	6.5	1.7
¥	8	8.2	1.74
China	1.62 [158]	2.04	1.23 [136, 137]
Asian	1.92 [159]	2.16	1.26 [Table 9.17]
Japan	2.03 [93]	2.22	1.28 [93]
India	2.41 [158]	2.58	1.38 [137]
Caucasian	2.57 [159]	2.50	1.36 [Table 9.17]
Brazil	3.19 [159]	3.05	–
African	5.93[c]	8.2	1.74 [Table 9.17]
W. Africa	6.33[d] [47]	–	–

£ assumed for model equation, € Japanese hair from Nagase et al. [93], ¥ from Porter et al. [47]
[a]From curl type DATA of Loussouarn et al. [159], de la Mettrie et al. [158] and Nagase et al. [93]
[b]Calculated from regression models by CRR from data of Porter et al. [47] and Nagase et al. [93]
[c]Subjects from: South Africa 141, Ghana 98, Kenya 47, Jamaica 50, US 85, N. Africa 133, from references [47, 158]
[d]Subjects from Ghana 35, Liberia 34 and Kenya 47 with highly coiled hair [47]

The reliability of this model is supported by the data of Table 9.27 showing a reasonable fit for the calculated Curl types which are generally within plus or minus 0.5 from the referenced STAM values; however for the one African sample the calculated value is off by 2.2 which may be due to a poor ellipticity value. More data is required to provide a better feeling for the real reliability of this model, however it should serve as a reasonable approximation. This model will likely work best for mean ellipticity values from more than 20 hairs for a hair sample rather than for individual hairs. The hair of the people of India by ellipticity and Curl type is more Caucasian-like than East Asian-like and the model confirms this observation which is consistent with genetic studies.

9.8.4 Variation of Curvature Across Populations and Countries

Table 9.28 summarizes data from the Loussouarn et al. [159] study by STAM for hair fiber curvature for three major geo-racial groups. The American Anthropological Association (AAA) issued a statement on race on May 17, 1998 stating that, "human populations are not unambiguous, clearly demarcated, biologically distinct groups" [169]. Furthermore the statement said, "Genetics indicates that most physical variation about 94% lies within so-called racial groups." The AAA

provided this relevant example [169], "Dark skin may be associated with frizzy or kinky hair or curly or wavy or straight hair".

It is true; linkage of hair fiber curvature to skin color alone just does not work. For example dark skinned people of African descent will most likely have very curly to kinky hair while similarly dark skinned people from northern India will most likely have very straight hair and many dark skinned people from southern India (sometimes called Dravidians) will have curly to wavy hair. But, if we link geographic origin, with racial origin and the tendency for skin color of the geo-racial group then the association with hair type increases markedly as shown by the data of Tables 9.24–9.29.

The following discussion considers curvature classification of hair fibers from more than 2,800 persons from the following references [47, 48, 129, 158, 159]. From these data sets we considered that Native Americans fit into the Asian group and that most other Americans can fit into one of the other three major geo-ethnic groups while most of the peoples of Europe, Asia and Australia also fit into these three groups.

The data of Table 9.28 shows that more than 90% of the African type hair examined is distributed primarily in Curl types V through VIII. Nevertheless, the hair of small percentages of panelists of African origin who are currently located in the United States and Northern African countries were classified in curl groups III and IV. Asian hair is most frequently found in curvature classes I through IV with a maximum percentage in group II. Caucasian hair is also found in groups I through IV, although the data shows it to be more of a Gaussian type distribution over these 4 curl types than for Asian hair.

From the data of Table 9.28 there appears to be a clean break for Asian and Caucasian hair between curl groups IV and V with virtually no persons above group IV from these two populations. Now if we consider geography alone, for the United States or Europe all eight curvature classes will be found. And if we consider skin color alone, all eight curl types will also be found. Therefore this summary of the data of Table 9.28 shows more meaningful distinction among hair curvature types can be made by considering geographic origin that I call

Table 9.28 Hair curvature by STAM for three major geo-ethnic groups from de la Mettrie et al. [158], Loussouarn et al. [159] and Porter et al. [47]

	Percentage of subjects with hair in STAM curvature grouping							
Hair type (No. subjects)[a]	I	II	III	IV	V	VI	VII	VIII
Asian hair N = 456	29	52	17	2	0	0	0	0
Caucasian hair N = 389[b]	12	35	37	16	0	0	0	0
African hair N = 554[c]	0	0.3	1.5	7	25.1	37	19.6	9.5

[a]Primarily from China, Japan, South Korea and Thailand [158, 159]. The percentages were estimated from graphs in the paper [159] since actual percentages were not provided

[b]Primarily from Denmark, France, Germany, Poland, Spain, UK and Russia [159]. The percentages were estimated from graphs in the paper since actual percentages were not provided

[c]Subjects from: South Africa 141, Ghana 98, Kenya 47, Jamaica 50, US 85, N. Africa 133, from references [47, 158]

Table 9.29 Curvature of Asian hair by country from study by De La Mettrie et al. [158] and Nagase et al. [93]

	Percentage of subjects with hair in STAM curvature grouping							
Country	I	II	III	IV	V	VI	VII	VIII
Korea N = 28	22	57	21	0	0	0	0	0
Japan[a] N = 40	13	67	20	0	0	0	0	0
Japan[b] N = 230	29	43	24	4	0	0	0	0
Thailand N = 65	19	46	32	3	0	0	0	0
China N = 213	45	48	7	0	0	0	0	0

[a]Data from de la Mettrie et al. [158]
[b]Calculated from curl radius data by Nagase et al. [93]

geo-ethnic or geo-racial groups than by considering either skin color or geographical regions alone.

The data of Table 9.29, constructed from the data of De La Mettrie et al. [158] and Nagase [93] shows hair curvature distributions from 4 different Asian countries. A concern is in the small sample numbers for the Korean and Japanese hair classifications by de la Mettrie, that is the number of subjects is so small that the total distribution is most likely not representative of the hair for those countries. This conclusion is reinforced by the data of Table 9.29. The De La Mettrie et al. data [158] of Table 9.29 from only 40 Japanese subjects shows hair classified in curl Types I, II and III only, while the data by Nagase et al. [93] measuring curl radius of hair from 230 Japanese subjects provides an average curl diameter of 8.8 cm and a distribution from 1.2 to 32 cm corresponding to a STAM curl classification over all four curl Types I to IV. The Nagase data also provides 43% in Curl type II while the de la Mettrie provides 67%. The average curl diameter (peak in the distribution curve) by Nagase et al. corresponds to curl type II which is the largest percentage Curl type found by de la Mettrie for Japanese hair also, see Table 9.29.

The data by Nagase [93], Hardy [48] and Kajiura et al. [166] are different studies where the curl radius was measured, while the study by Porter et al. [47] measured curl diameter, but STAM was not used for classification of hair curvature in the manuscripts of these later four studies. Therefore, I converted curl radius to curl diameter for Table 9.30 and classified the data by the STAM procedure showing good agreement with expectations. For the data by Syed et al. [44] I calculated the cross-sectional area and ellipticity and used the equations above to approximate the Curl type between curl classes IV to VIII.

This type of hair fiber curvature classification can be done conveniently from curl radius or curl diameter data for curl types I through V and from ellipticity data for Curl types I through VIII.

The conversion of curl radius or diameter or ellipticity from different laboratories to the STAM hair curvature types of Table 9.30 provides good agreement with the classifications found by De La Mettrie et al. [158] and Loussouarn et al. [159] and illustrate the robustness of the STAM method. Because it is robust enough to permit comparisons across different laboratories

Table 9.30 Comparison of hair from different laboratories/studies by STAM curl method

Study	Asian		Hair		Caucasian		Hair		African		Hair	
	N	Est CD	Type	Country	N	Est CD	Type	Country	N	Est CD	Type	Country
Nagase [93]	230	1.2–32	I to IV	Japan								
Hardy [48]	30	12–45	I	Japan	30	3.2–18	I–III	NWEurope	20	0.2–0.32	V–VIII	EAfrica
Kajiura [166]	2	1.8–18.6	I to IV	Japan	2	3.6–12	I–III	Australia	1	0.36–0.56	V–VIII	USA
Syed [44]									Not given		VII–VIII	USA
Porter et al. [47]									5	0.2–1.2	V–VII	USA

as shown by these curl assignments in Table 9.30, it allows useful curvature distinctions. Furthermore, because of the large database provided by de la Mettrie et al. and Loussouarn et al., I recommend that our industry adopt this method (or a minor modification of it) for future hair fiber curvature comparisons. Wherever possible in this book I have tried to refer to hair curvature comparisons by the STAM hair curvature types.

9.9 Water (RH), pH and Solvents and the Dimensions of Hair

9.9.1 Hair and Wool Have Similar Water Binding Amounts and Groups

Stam et al. [122] used a microscopic method to measure changes in the length and diameter of human hair fibers at different RH's and calculated changes in cross-sectional area and volume (see Table 9.31). These data show a small increase in fiber length and a large increase in diameter with increasing RH. This swelling behavior of hair is related to its fundamental structure as described in Chap. 1 in the section entitled, *Swelling Behavior of Hair*.

Although the swelling behavior of keratin fibers is usually explained in terms of its intermediate filament-matrix components, Swift [170] and others have provided evidence that the non-keratin portions of hair may also be important to fiber swelling. For example, Swift demonstrated by microscopic studies involving the penetration of fluorescent labeled proteins into hair in an aqueous medium that a large order swelling occurs in the non-keratin regions of hair. The diameter swelling of hair by water from the dry state is usually given as about 14–16%. On the other hand, X-ray diffraction measurement of intermediate filament separation distances by Spei and Zahn [171] indicates that swelling of only 5.5% occurs in these regions.

Swift [169] therefore proposed that the difference may be explained by the large order swelling that occurs in the non-keratin regions of hair, primarily the endocuticle and the cell membrane complex of hair. However, greater swelling is

Table 9.31 Dimensional changes of human hair versus RH [122]

% RH	Moisture absorption			
	% increase in diameter	% increase in length	% increase cross-sectional area	% increase in volume
0	0	0	0	0
10	2.3	0.56	4.7	5.7
40	5.1	1.29	10.5	12.2
60	6.9	1.53	14.3	16.3
90	10.6	1.72	22.3	24.6
100	13.9	1.86	29.7	32.1

expected in the keratin associated proteins than the intermediate filaments. For additional details on hair swelling, see Chap. 1.

The hysteresis in the moisture absorption-desorption curves of keratin fibers is an interesting phenomenon. At any given RH between 0% and 100%, human hair contains less water when absorbed from the dry state compared to when it undergoes desorption, that is when it loses water from the wet state (see Table 9.32). Chamberlain and Speakman [36] observed this phenomenon earlier for human hair and Speakman [37] observed it for wool fiber (see Table 9.33). Additional water binding when the hair is wet occurs because certain groups in hair that are capable of binding water are not accessible to water vapor from the shrunken dry state. On the other hand, when the hair is highly swollen with liquid water these groups are accessible and water binds to them.

Stam et al. [122] found that tension on hair fibers influences their dimensions (moisture content) at different RH's. For example, stretching hair fibers below 60% RH provides less swelling than for un-stretched hair, while stretching hair at RH above 60% provides more swelling than un-stretched hair.

Table 9.33 shows that moisture loss (desorption) and regains (absorption) for human hair and wool fiber are virtually identical. It has been suggested [30] that the moisture regains of human hair and wool fiber are virtually identical up to about 90% RH, where they diverge wool to a regain of 33%, and hair to about 31%, the difference most likely due to the higher cross-link density in human hair. However, even if divergence does occur, the actual difference in moisture regain by these two fibers is relatively small which suggests that to a large extent the same functional groups are responsible for water binding in hair and wool fiber.

Table 9.32 Absorption verses desorption of moisture [122]

% RH	Absorption % increase in volume	Desorption % increase in volume
0	0	0
10	5.7	6.8
40	12.2	13.0
60	16.3	17.3
90	24.6	25.1
100	32.1	32.1

Table 9.33 Water content of human hair and wool fiber versus RH

% RH	Human hair (weight gain) [36]		Wool (weight gain) [36]	
	% absorption	% desorption	% absorption	% desorption
0	0	0	0	0
8	3.9	5.1	–	–
35	–	–	8.4	9.7
40	10.2	12.0	–	–
63	14.8	16.7	14.3	–
86	22.6	23.3	–	–
100	31.2	31.2	31.9	31.9

The rate of moisture regain is considerably slower from water vapor than from liquid water (diffusion-controlled reaction). Liquid water at room temperature will penetrate the hair in less than 15 min and in <5 min at 92°F (~33°C) [122], whereas 18–24 h is required for single fibers to equilibrate in a humid atmosphere, with even longer times for a fiber assembly as shown by Steinhardt and Harris [172].

9.9.2 Variation of Fiber Surface Area with Diameter

For a given weight of hair, the fiber surface area is inversely proportional to the fiber diameter. Table 9.34 shows how the calculated fiber surface area varies with diameter for 1 g of hair (assuming it is a right cylinder).

9.9.3 The Swelling of Human Hair Changes with pH

The swelling of human hair in aqueous solutions after 24 h or longer at different pH values exhibits four distinct parts [109–111] (Fig. 9.14):

1. A minimum in swelling from pH 4–9
2. Above pH 10, a large increase in swelling
3. pH 3–1, a slight increase in swelling
4. Below pH 1, a slight decrease in swelling

The minimum in swelling from pH 4–9 is consistent with the observation of Steinhardt and Harris [172]. In the absence of added electrolyte, there is no combination of wool fiber with mineral acid or alkali from pH 5 to 10. This is in the vicinity of the isoionic point of hair (the neutral point for the total fiber, which is when the number of positively charged and negatively charged groups is equal). The large increase in swelling above pH 10 is largely due to ionization of diacidic amino acid residues in the hair and partly due to keratin hydrolysis. The increase in swelling from pH 3 to 1 is due to the combination of acid with the dibasic amino acids. Breuer [75] attributed the decrease in swelling below pH 1 to an irreversible structural change.

Ehrhardt (private communication) observed alkaline swelling in 0.1 N NaOH after only 5 min of reaction with hair at 95°F (~35°C). Under these conditions, a

Table 9.34 Fiber diameter and surface area

Fiber diameter (μm)	Calculated[a] surface area (cm^2 for 1 g hair)	Calculated relative surface area
40	758	3.0
80	379	1.5
120	253	1.0

[a]For 1 g of hair, assuming it is a right cylinder

similar effect was not observed using 0.1 N hydrochloric acid. The swelling of human hair in acid below pH 3 is slightly less than that of wool fiber [114], and has been attributed to the higher cross-link density of human hair [34, 114].

9.9.4 Solvents and Swelling of Human Hair

Valko and Barnett [74] and Barnett [121] showed that acetonitrile, triethyl-phosphate, and glycerol swell hair to a lesser extent than water. In fact, glycerol is sometimes used in tensile or torsional testing to approximate 0% RH [25] because of the lack of hair swelling when hair fibers are immersed in this solvent. Dimethyl formamide, ethylene glycol monomethylether, and diethylene glycol monomethylether swell hair similar to water, although the rate of swelling by these solvents is slower than the rate of swelling by water [74, 121]. Glacial acetic acid and formic acid swell hair to a greater extent than water [74, 121]. Formamide and urea (aqueous solutions of urea) also produce swelling beyond that of water, probably by promoting greater cleavage of hydrogen bonds than produced by water [66, 121].

Amines such as ethyl amine, at 25% in water or higher concentrations, swell hair to a greater extent than water. These solutions rupture peptide and amide linkages and ultimately disintegrate (dissolve) the hair (after several days) [74, 121]. Concentrated solutions of alkali halides (25–60%), after several days, produce extensive dimensional changes to hair [74, 121]. Barnard and White [114] found extensive swelling by potassium iodide, sodium bromide, lithium bromide, and lithium chloride solutions, but not for sodium chloride. Those halide salts that produce extensive swelling of human hair are believed to be capable of breaking hydrogen bonds that water alone is incapable of breaking. For additional details on this subject, see the section on supercontraction in Chap. 4.

9.9.5 Hair Swelling by Permanent Wave Agents

Shansky [173] developed a special cell to follow hair swelling under the light microscope. He used this system to study permanent-wave reactions with human hair and found that the reduction step produces an increase in diametral swelling which increases with increasing disulfide bond rupture [173, 174]. Shansky also found that rinsing with water, after reduction, produces additional swelling. He attributed this effect to osmotic forces, since there is a lower salt concentration outside the fibers after rinsing. Neutralization then reverses swelling. This de-swelling effect is caused by the reformation of disulfide cross-links [173, 175].

Ekstrom [116] described a moving boundary between swollen and un-swollen fiber as the reducing front penetrates the hair during permanent waving and

depilation. Keil [176] using the polarizing microscope noted a similar moving boundary in his studies on permanent waving. Wickett [177] studied the reduction of hair with sodium thioglycolate above pH 10 when diffusion of the mercaptan into the hair is rate-controlling and demonstrated moving boundary kinetics. However, for reaction at lower pH values (below pH 9), the nature of this reaction depends on the reactivity of the particular individual's hair. For one individual whose hair was highly reactive, the reaction followed pseudo-first-order kinetics. In this situation, the permanent wave was reaction-controlled. However, for another individual's hair (difficult-to-wave hair) the reaction exhibited moving boundary kinetics.

Powers and Barnett [174] found that a large excess of reducing solution at pH 10 (for reduction times of 15 min or longer) produced swelling in excess of 200% and effectively destroyed the hair. They also found that the amount of swelling increased with increasing pH from 8 to 10. This effect is related to the increasing rate of disulfide rupture with increasing pH. Finally, these scientists indicated that the effectiveness of the neutralization step in permanent waving could be assessed by relating it to the swelling action of hair in water. In general, hair swelling methods have been valuable for providing information about chemical alterations to human hair, relevant to permanent wave reactions. For additional details see Chap. 4.

9.9.6 Swelling Test for Hair Damage

Klemm et al. [178] described a swelling test to assess hair damage by permanent waves and bleaches. This test consists of measuring hair fiber diameter swelling in a series of three solutions: the first treatment is water for 10 min; the second, 60% lithium bromide for 60 min; and the third, water for 10 min. From an empirical equation, numerical values of swelling behavior may be calculated. This method distinguishes between single and multiple permanent waves and between single and multiple bleaches on hair. It essentially compares swelling in water versus lithium bromide, one of the most effective hydrogen bond breaking agents know. The results rely on the fact that the more damaged a hair fiber the more hydrogen bonds are capable of being broken by this powerful hydrogen bond breaking agent.

9.10 Hair Fiber Friction

Friction is the force that resists motion when one body slides over another. The classical laws of friction were formulated by Leonardo da Vinci and later by Amontons, with whom they are generally associated. Amontons Law states that

the frictional force necessary to slide one surface over another is proportional to the normal load pressing the two surfaces together (W).

$$\text{Frictional force} = \mu W$$

The proportionality constant (μ) is called the coefficient of friction. The frictional coefficient is generally independent of the area of contact. At low loads, when the fiber undergoes a large amount of deformation the true area of contact changes significantly. Thus, at low loads, the area of contact affects the coefficient of friction. The force necessary to initiate movement determines the coefficient of static friction (μ_s). The force necessary to maintain movement when the body is in motion determines the coefficient of kinetic friction (μ_k). μ_k is almost always less than μ_s.

These laws of friction apply to dry, un-lubricated surfaces and to boundary lubricants (very thin solid or nonfluid films separating the surfaces). But, these laws do not apply to hydrodynamic lubricants [179], such as fluid layers that separate the moving surfaces (for example, engine-lubricating oils). Generally, lipid on the surface of the hair provides a reduction in friction. This is an experimental variable of concern to control. For example, by careful cleansing of the test surfaces of the fibers or by testing in surfactant solutions this variable may be controlled. There are several theories attempting to explain friction. For discussion of these theories, see the book by Howell et al. [180], *Friction in Textiles.*

Two important variables relevant to friction on hair are relative humidity (or moisture content of the hair) and the normal load (W) pressing the two surfaces together. It is helpful to consider friction on hair in terms of two conditions for relative humidity and two conditions of load, thus forming the 2 × 2 matrix below.

		Low RH (60% RH or lower)	High RH (in water)
↑	High (g)	Dry high load	Wet high load
Load	Low (mg)	Dry low load	Wet low load
	Relative humidity →		

The dry high-load condition is the state that simulates hair friction conditions relevant to dry combing or brushing of hair. The wet high-load condition is relevant to wet combing. On the other hand, the dry low-load condition is relevant to those critical hair-on-hair interactions involved in style retention and hair body. Robbins [181] described three different experimental conditions to characterize hair fiber friction by these three relevant humidity-load conditions. These three approaches are summarized in the next section.

9.10.1 Methods for Measuring Friction on Hair Fibers

Two different capstan methods (a fiber over a rod) have been used to measure frictional coefficients of single hair fibers [182, 183] at high load both in air (low RH) and in aqueous media. The apparatus used by Schwartz and Knowles [182] involves draping a fiber with equal weights on each end over a cylinder. One weight is placed on a torsion balance to measure the frictional forces developed as the cylinder is moved against the fiber.

The method of Scott and Robbins [183] involves attaching the root end of a hair fiber to the load cell of a device such as an Instron tensile tester. The fiber is weighted at the tip end and partially wrapped around two mandrels (these may be rotated) but more relevant results are obtained when the mandrels are not rotated. The mandrels are attached to the crosshead. As the crosshead moves downward the mandrels are rubbed against the fiber and the frictional load is recorded. In a capstan system (such as this), the coefficient of kinetic friction (μ_k) may be calculated from the following expression:

$$\underline{\mu}k = \frac{1}{\phi'} \ln \frac{T_2}{T_1}$$

where ø is the angle of wrap in radians, T_2 is the tension after passing over the rod, and T_1 is the tension before passing over the rod. This equation assumes that friction is independent of load, a condition valid for the load ranges used in these two studies of frictional effects on human hair. Scott and Robbins used a 1 g load (high load, on the tip end of the hair) small enough so that the total load (weight plus frictional load) did not exceed the fiber yield point.

Different rubbing speeds (in the vicinity of 10 in. per minute or higher) do not appreciably change the friction coefficient [183]. However, Robbins [181] demonstrated that friction increases with decreasing rubbing speed in the vicinity of 0.5 in. per minute and it appears to level near 0.05–0.02 in. per minute, probably approaching static friction. At these lower rubbing speeds, greater differences can be demonstrated between treatments, especially on dry hair. Therefore, the preferred laboratory conditions for simulating the actions involved in wet combing of hair involve a load of approximately 1 g/fiber, with the fiber immersed in water, at a low rubbing speed in the vicinity of 0.02 in. per minute. To simulate dry combing, the preferred conditions are also a load of approximately 1 g per fiber, near 60% RH, and a low rubbing speed of approximately 0.02 in. per minute.

Wrap angle changes produce significant differences in friction, as indicated by the capstan equation above. Thus, the friction coefficient increases with increasing wrap angle. The above two friction methods measure coefficients of kinetic friction and the low rubbing speed system approaches static friction. Since Amontons law states that static friction is generally higher than kinetic friction, there is probably a directional similarity between static and kinetic friction.

Robbins [181] also developed a procedure for determining dry static friction at low load (in the milligram range) by modification of the incline plane fiber loop method of Howell and Mazur [184]. This procedure attempts to measure those intimate fiber-fiber interactions associated with hair body and style retention. The procedure involves determining the angle of slip for a small hair fiber loop sitting on two parallel hair fibers. Above 1 mg load, the friction coefficient decreases very slowly with increasing load. However, below 1 mg load, the friction coefficient increases abruptly with decreasing load (see Fig. 9.29). The diameter of the fiber loop (in the vicinity of less than 2 cm) affects the friction coefficient. Presumably this effect is due to scale distortion as the loop becomes progressively smaller resulting in an increase in the true area of contact (A) as described by this equation:

$$F = AS$$

A = true area of contact

S = shear strength of materials in contact

Larger hair fiber loops are recommended (in the vicinity of 5 cm diameter) providing a load of 1–2 mg, depending on fiber thickness. At low load (mg range), the fiber system is sensitive to cohesive/viscosity forces from thick layers of product deposits, because the fiber system at such low loads has difficulty ploughing through thick viscous deposits. For example, a pomade-type combing aid (consisting of petrolatum and mineral oil) was evaluated and shown to dramatically increase the apparent friction coefficient at low load due to the cohesive nature of the viscous pomade. However, when this same pomade was tested by a high-load dry friction method, the friction coefficient decreased relative to the untreated control fibers. These effects show that this pomade will hold fibers of an assembly

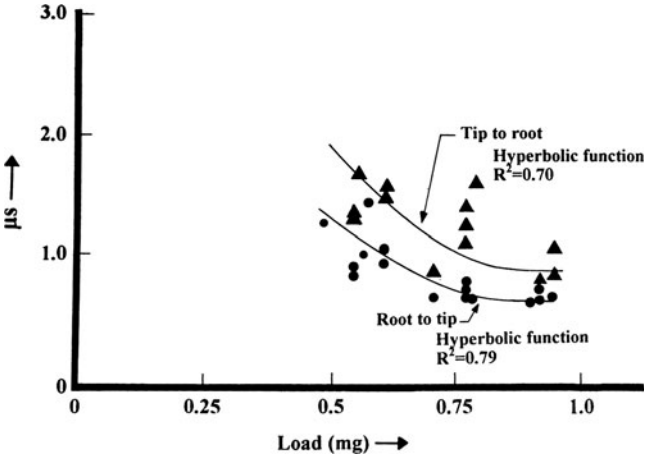

Fig. 9.29 The directional nature of the frictional coefficient of human hair and its variation with load (at 60% RH)

in place better, because fiber movement at low-load forces (mg range) will be resisted by the cohesive forces of the viscous pomade ingredients. However, when high-load forces are applied as in combing, a viscous product can act as a lubricant and thereby facilitate comb on hair and hair on hair movement. This experiment verifies the need for both low- and high-load friction methods to develop a more complete understanding of hair product behavior. Other approaches to measure fiber friction are described in the books by Howell et al. [180] and Meredith and Hearle [185].

9.10.2 Relative Humidity and Friction

As indicated above, wet friction for human hair is higher than dry friction (see Table 9.35). In addition, both static and kinetic friction and the differential friction effect increase with increasing RH, that is with increasing water binding by the hair. These same phenomena have been observed for wool fiber [186, 187].

9.10.3 Friction and Fiber Diameter

Scott and Robbins [183] found that high-load friction is independent of hair fiber diameter. This effect agrees with theory and with the results of Fishman et al. [188]. However, Martin and Mittleman [189] reported a slight increase in friction with wool fiber diameter. For low-load hair on hair friction, the fiber diameter effect is difficult to test, because as fiber diameter increases, the load also changes and thus the friction coefficient changes.

9.10.4 The Directional Friction Effect

As with most animal fibers, human hair shows a directional friction effect, that is, it is easier to slide a surface over hair in a root-to-tip direction than in a tip-to root-direction (see Figs. 9.29 and 9.30). This directional friction effect is useful for orienting hair fibers for experimentation. For example, take a hair fiber between the thumb and forefinger, and gently rub back and forth along the fiber axis. If rubbing

Table 9.35 Friction coefficients for hair on comb substrates (high-load condition) [182]

Coefficient of kinetic friction			
	Hard rubber	Nylon	Aluminum
Dry	0.19	0.14	0.12
Wet	0.38	0.22	0.18

Fig. 9.30 SEM of a knotted hair fiber, illustrating the cuticle cell surface structure. Note the raised scales caused by the severe bending stress of the knotted fiber

is done correctly, the fiber will move in the direction of the root end or one will note that it is easier to rub over the hair in the root to tip direction. Moistening the fingers makes this effect even more apparent, because the differential friction effect increases with increasing moisture in the fiber surface layers.

Table 9.36 illustrates this effect when rubbing hair fibers against a hard rubber surface in dilute shampoo and creme rinse solutions. Note that the differential friction effect is greater in the creme rinse solution than in the test shampoo. This is because the test creme rinse lowered the root-to-tip friction coefficient more than it lowered the tip to root coefficient.

Scott and Robbins [183] and Schwartz and Knowles [182] examined root to tip rubbing in more detail, because the friction coefficient for root to tip rubbing is lower than tip to root rubbing and it produces less abrasive damage to the hair.

Swift and Bews [190] suggested that totally or absolutely dry wool fiber (0% RH) does not display a differential friction effect (absolutely dry wool against a glass surface). However, Swift pointed out that absolutely dry wool is a hypothetical condition. King [186] demonstrated a differential friction effect (DFE) from dry wool against horn, and Robbins [181] for human hair against hard rubber. The DFE does become smaller with decreasing RH, but whether or not the DFE disappears

Table 9.36 Directional friction effect for human hair at high load (Scott, private communication)

	High cleaning shampoo (μ_k)	Creme rinse (μ_k)
Rubbing root to tip (μ_1)	0.425	0.293
Rubbing tip to root (μ_2)	0.546	0.475
Directional friction effect (DFE)	0.285	0.621

$\text{DFE} = \frac{\mu_2 - \mu_1}{\mu_1}$

completely at absolute zero RH is academic. Swift and Bews [190] proposed the following explanation to account for the decreasing DFE with decreasing water content in animal hairs.

The two major layers of cuticle cells, the exocuticle and endocuticle, may be expected to behave differently with respect to moisture regain. The exocuticle, because of its high cross-link density, should not swell so readily as the endocuticle, with its paucity of cross-links and high density of ionic groups. Swelling of the endocuticle on regain could convert it to a gel-like structure which could contribute to the DFE in animal hairs [180, 185, 187, 191].

9.10.5 Mandrel and Comb Composition and Fiber Friction

Both Scott and Robbins [183] and Schwartz and Knowles [182] found wide variation in the coefficient of kinetic friction for rubbing human hair fibers against different mandrel compositions. Some of Schwartz's results are summarized in Table 9.35. Most interesting are the relatively low values on aluminum, suggesting a benefit for aluminum combs. However, Wolfram and Hambidge [192] determined that the frictional characteristics of combing materials are not a very important factor in hair combing. This result suggests that hair on hair friction the cause of tangles and snags is more important to combing forces than hair on comb friction.

Experimentally, it is generally easier to test friction of hair against another substrate than to test hair-on-hair friction. It is likely that the relative frictional effects of hair against rubber or another substrate will correlate well (but not perfectly) with hair-on-hair friction, as evidenced by the results of Table 9.35 showing lower dry than wet frictional coefficients for all substrates.

9.10.6 Normal Room Temperatures do not Affect Hair Friction

Scott and Robbins [183] found that temperature changes from 75 to 110°F (~24–43°C) produced virtually no changes in the high-load friction coefficient. Other temperature ranges have not been reported.

9.10.7 Bleaching (Oxidation of Hair) Increases Hair Friction

Scott and Robbins [183] demonstrated that bleaching hair increases hair fiber friction. Furthermore, friction increases with increasing bleach damage. This same effect has been observed both at high load and at low load. The results of Table 9.37, in "shampoo" illustrate this effect, while those in conditioner illustrate the effect of conditioners on bleached hair. These results suggest that the stronger

Table 9.37 Effect of bleaching on hair fiber friction [183] (high load)

	μ_k in shampoo	μ_k in conditioner rinse
Unmodified hair	0.249	0.220
1 × mild bleach	0.342	0.190
3 × mild bleach	0.427	0.193

interaction of bleached hair with cationic conditioner ingredients is consistent with the higher concentration of ionized cysteic acid groups at or near the surface in bleached hair [53]. The influence of bleaching and its frictional effects on the cosmetic properties of hair are discussed in Chap. 10.

9.10.8 Permanent Waving Increases Hair Friction

Permanent waving not only changes hair fiber curvature, but it also increases hair fiber friction [182]. The influence of permanent waves on cosmetic hair assembly properties is discussed in Chap. 10.

9.10.9 Shampoos and Hair Friction

Table 9.38 summarizes some of the data of Scott and Robbins [183] for the wet friction coefficients of shampoos at high load. The coefficient of friction for hair fibers treated with the high conditioning shampoo is lower than for hair treated with the high cleaning shampoo. This effect suggests easier wet combing by the conditioning shampoo and has been verified.

9.10.10 Conditioners and Hair Friction

From friction behavior versus concentration of different cationic types, Scott and Robbins [183] suggested three types of cationic conditioner ingredients. Table 9.39 illustrates this behavior in which the cationics were tested by determining the friction coefficient of hair fibers against hard rubber first in the higher concentration solutions (0.1% and 0.01%) and then simply by changing solution to deionized

Table 9.38 Friction coefficients by shampoos [183] (high load)

	Hair on hard rubber (μ_k)
High cleaning shampoo	0.342
Experimental high conditioning shampoo	0.155

Table 9.39 Influence of cationic concentration and rinsing effects on hair friction [183]

	Concentration		
	0.1% μ_k	0.01% μ_k	0%[a] μ_k
Cetrimonium bromide (CTAB)	0.390	0.298	0.537
Stearalkonium chloride (SBDAC)	0.450	0.394	0.298
Distearyldimonium chloride (DDAC)	0.171	–	0.298
Imidazolinium quaternary (IQ)	0.188	0.169	0.166

[a]This point was determined after the higher concentration (0.1%) simply by changing solution to deionized water, to simulate rinsing

water, to simulate rinsing. For CTAB, the friction coefficient decreased with concentration from 0.1% to 0.01%. For a "simulated rinse" (0%), it increased, indicating that CTAB is not bound tightly to the hair fiber surface.

SBDAC illustrates another type of behavior, where friction decreases with concentration; however, on rinsing to 0% it remains low. Both IQ and DDAC illustrate the third type of behavior, where the friction coefficient is low under all test conditions. These data suggest a point of superiority for DDAC and IQ over CTAB. The decrease in the friction coefficient with concentration and with rinsing for SBDAC is unexpected. These results indicate the necessity for thorough rinsing with this ingredient for optimum conditioner performance.

Scott and Robbins [183] tested CTAB above and below its critical micelle concentration, using salt to promote micelle formation. No significant difference was found in the friction coefficient, suggesting that molecular sorption rather than micellar sorption occurs to affect the friction coefficient in systems of this type. For additional discussion of conditioners and the effects of reduced fiber friction on hair properties, see Chap. 10.

9.11 Mechanical Fatiguing, Extension Cycling and Scale Lifting

Kamath et al. [193] of Textile Research Institute in Princeton tested mechanical fatiguing of human hairs by employing loads of 20–40 grams (generally 30 g) for a fixed number of cycles up to 100,000. Controlled humidity and temperature is a requirement for this type of testing as for most hair fiber testing. At 30 grams load, the strain is generally just beyond the Hookean region and is similar to "some" of the strains encountered in combing and brushing of hair [194] where repetitive or cyclic stresses occur at very rapid strain rates. Mechanical fatiguing is essentially impact loading hundreds to thousands of times [193–196]. A hair fiber with an attached weight can be impacted either by fatiguing (many times) or against another object such as another hair fiber or a comb tooth (once or a few times) and is described in Chap. 10 and in two publications by Robbins [14, 195].

Extension cycling on the other hand has been used by Gamez-Garcia [16] where he employed strains of 10–30% under conditions of controlled humidity and

temperature, generally for 50–200 cycles. Gamez-Garcia found the most damaging effects to the cuticle at low relative humidity produced microscopic damage with strains as low as 10% stretch.

These methods (fatiguing, extension cycling and impact loading) are relatively new (compared to tensile testing) and they simulate "some" of the damaging actions and effects from combing and brushing. Tensile testing is useful for investigating changes to the cortex of the fiber from treatments or physical actions. But, tensile testing is not so meaningful in terms of simulating the stresses normally encountered by hair fibers on consumers' heads because hair fibers are not normally stretched 25–50% of their length or at exceedingly low strain rates as employed in most tensile tests. Furthermore, the fact that cuticle damage cannot be detected by tensile testing is another important negative. However, torsional testing can reveal cuticle damage. The following discussion illustrates some of the results from these newer test methods.

Cyclic stretching and fatiguing of hair fibers occurs in everyday grooming actions and these actions ultimately lead to cuticle deformation and cuticle fragmentation (Figs. 9.31–9.35).

Gamez-Garcia [16] demonstrated that cuticle cracks in the non-keratin regions can be induced by only 10% extension at low humidity (Fig. 9.31) creating cracked and lifted scales. He also showed that the extent of crack formation depends on the number of cycles. Kamath et al. [193] observed similar findings for mechanical fatiguing of hair fibers. Figure 9.32 illustrates the effects of fatiguing on the cuticle and Figs. 9.33 and 9.34 shows the effects on the cuticle and the cortex of hair by fatiguing followed by stretching the fibers to break.

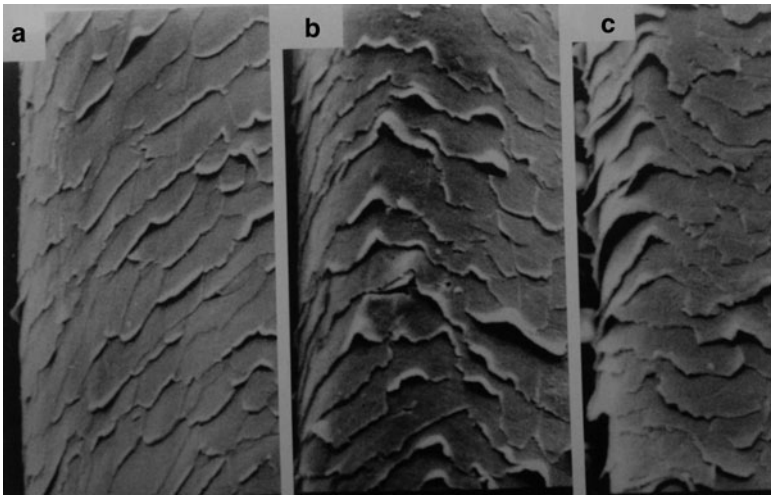

Fig. 9.31 Scale lifting caused by extension cycling to 10% at 10% RH [16]: (**a**) to 50 cycles, (**b**) to 100 cycles and (**c**) to 200 cycles from Gamez-Garcia [16] (reprinted with permission of the Journal of the Society of Cosmetic Chemists)

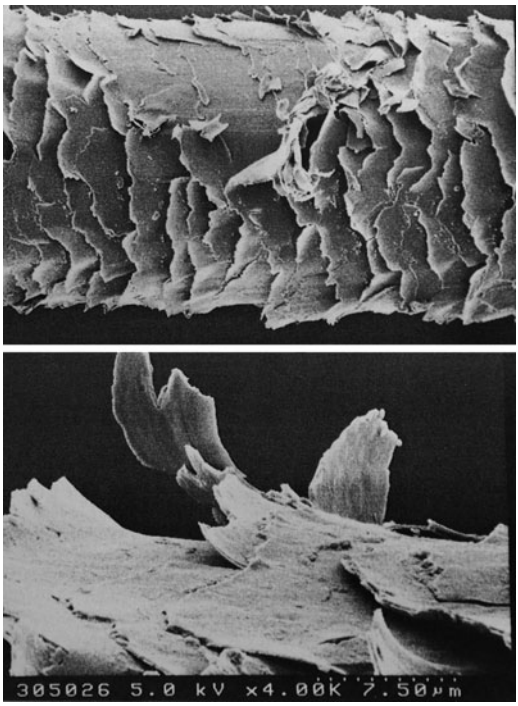

Fig. 9.32 Scale lifting caused by fatiguing chemically undamaged hair to 100,000 cycles with a 30 g load in 31 h and then extended just below the failure load. Electron micrographs at two different magnifications kindly provided by Sigrid Ruetsch

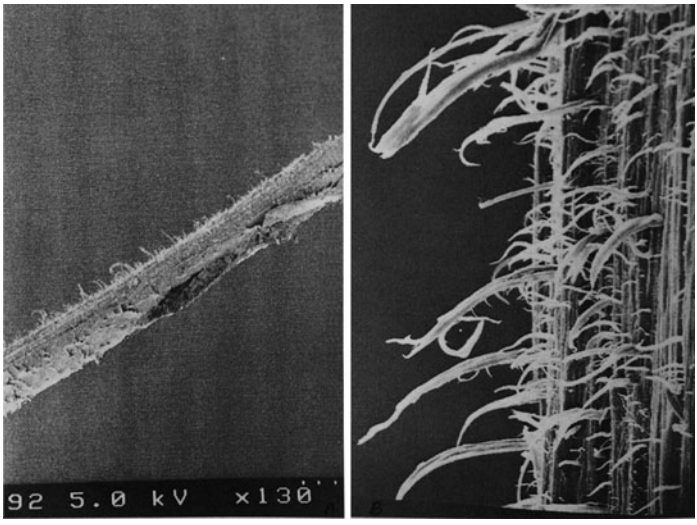

Fig. 9.33 Fiber fatigued to 100,000 cycles with a 30 g load in 31 h and then extended. Note the severe fracture effects causing the separation of cortical cells indicating weakening of the cell membrane complex. (**a**) Low magnification. (**b**) High magnification. SEMs kindly provided by Sigrid Ruetsch

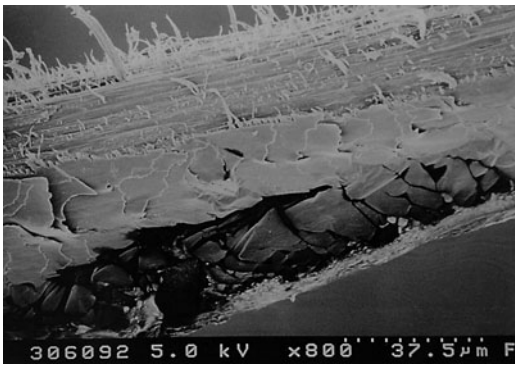

Fig. 9.34 Fiber fatigued to 100,000 cycles with a 30 g load in 31 h and then extended to break (near the fracture site). Note the severe cuticle cracking and lifting in addition to the separation and lifting of cortical cells. SEM kindly provided by Sigrid Ruetsch

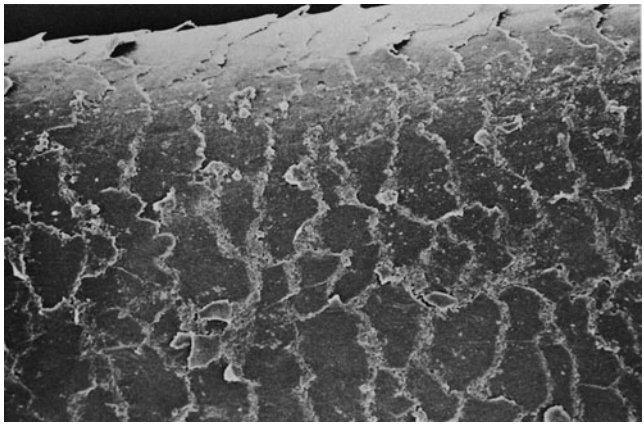

Fig. 9.35 Hair fiber chemically bleached with alkaline peroxide and then fatigued. Note the severe chipping and crumbling of the cuticle scale edges. Contrast this effect to that of Fig. 9.5 (*top*) involving no chemical bleaching. SEM kindly provided by Sigrid Ruetsch

The process of cuticle loss or fragmentation was described in detail in Chap. 6. A mechanism was also presented to explain this phenomenon. Chemical or physical attack to the cell membrane complex and the endocuticle weakens these vital regions producing increased swelling and even cracks that accelerate the processes of fragmentation and in some cases catastrophic failure. Penetrating chemicals can enter damaged areas more rapidly. Certain chemicals either strengthen the fiber (not often) or more likely produce scale lifting and/or distortion and in this manner either inhibit or accelerate the process of cuticle degradation and scale removal. The next section of this manuscript describes the effects of penetrating ingredients on the cell membrane complex and the endocuticle and the consequences of these actions using the techniques of mechanical fatiguing and extension cycling coupled with microscopy.

If cuticle cracks are formed by stretching or fatiguing and the fibers are treated with water and dried, the scales sometimes return to their "normal" appearance at a microscopic level. However, subsequent treatments (other than water) to cracked or damaged scales can either inhibit further damage or accelerate cuticle fragmentation. Even pre-treatments can affect fragmentation.

Gamez-Garcia [16] determined that pre-treatment of hair fibers with hydrogen bonding plasticizers such as glycerine or propylene glycol (without rinsing) inhibits scale lifting from extension cycling. These effects may be similar to the effects of pre-shampoo treatments with oils such as coconut oil which has been shown by Ruetsch et al. [197] to reduce cuticle fragmentation.

Hilterhaus-Bong and Zahn [198] demonstrated that intercellular lipids can be extracted from hair by multiple detergent washings. Gould and Sneath [199] examined root and tip sections of scalp hair by transmission electron microscopy (TEM) and observed holes or vacancies in the thin cross-sections. These holes (cracks) were attributed to breakdown and removal of intercellular components by shampoos. Removal of parts of the cell membrane complex by shampoos will weaken this domain making the hair more susceptible to cuticle fragmentation. This effect is consistent with the finding in our laboratories that cuticle fragmentation and protein loss (see Chap. 6) is greater in the tip ends of hair fibers treated only with shampoos and no other cosmetic treatment.

Polymer JR-400 when applied to fatigued or stretched hair inhibits cuticle scale lifting. This effect is illustrated by comparing Fig. 9.35 (bleached, fatigued control fiber) to Fig. 9.36 (bleached, JR treated, fatigued). Note the breakage and crumbling of the scales at the cuticle edges in the control versus the fewer broken scale edges of the treated fiber of Fig. 9.36. This effect is illustrated further by comparing Figs. 9.37 (bleached, fatigued and extended control) and 9.38 (bleached, JR treated,

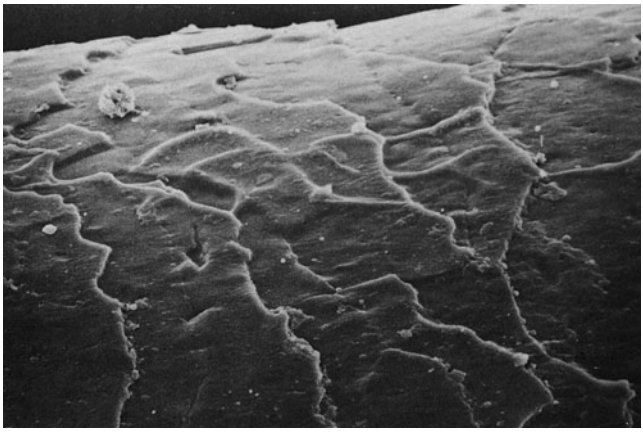

Fig. 9.36 Hair fiber chemically bleached with alkaline peroxide then treated with Polymer JR-400 solution and then fatigued 100,000 times with a 30 g load. Note virtually no scale lifting or crumbling of the cuticle scale edges compared to that of Figs. 9.35 and 9.37. SEM kindly provided by Sigrid Ruetsch

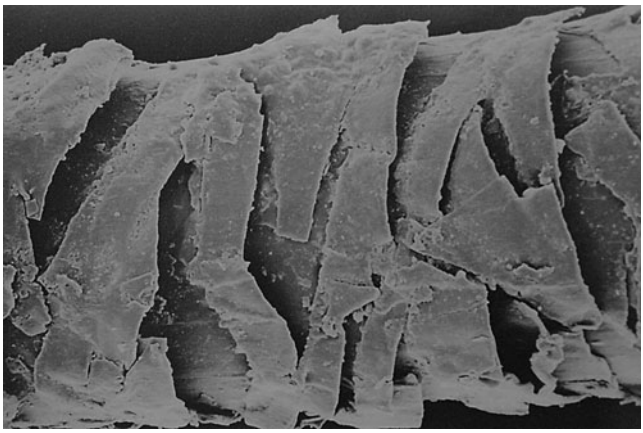

Fig. 9.37 Hair fiber chemically bleached with alkaline peroxide then fatigued 100,000 times with a 30 g load and then extended. Note the extensive scale lifting and fracturing underneath the scales at the weakened cell membrane complex. SEM kindly provided by Sigrid Ruetsch

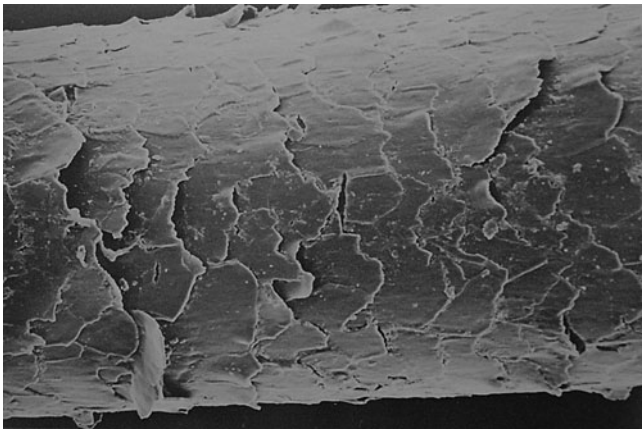

Fig. 9.38 Hair fiber chemically bleached and treated with Polymer JR-400, then fatigued and extended. Note the minimal scale lifting compared to the micrograph of Fig. 9.37. SEM kindly provided by Sigrid Ruetsch

fatigued and extended). Note the large difference in the cuticle scale lifting of Fig. 9.37 versus that of the JR treated hairs in Fig. 9.38.

Post treatment of extension cycled hair with 3% aqueous solutions of polymers such as a hydrolyzed wheat-polysiloxane copolymer or a protein-silicone copolymer inhibits scale lifting that can be induced by additional bending after extension cycling (Fig. 9.39) [16]. On the other hand, polymers such as polyethylene-imine (3%) fail to prevent scale lifting from additional fiber extension. But, blow drying of polyethylene-imine treated hair produces cuticle lifting and distortion (Fig. 9.40) [16].

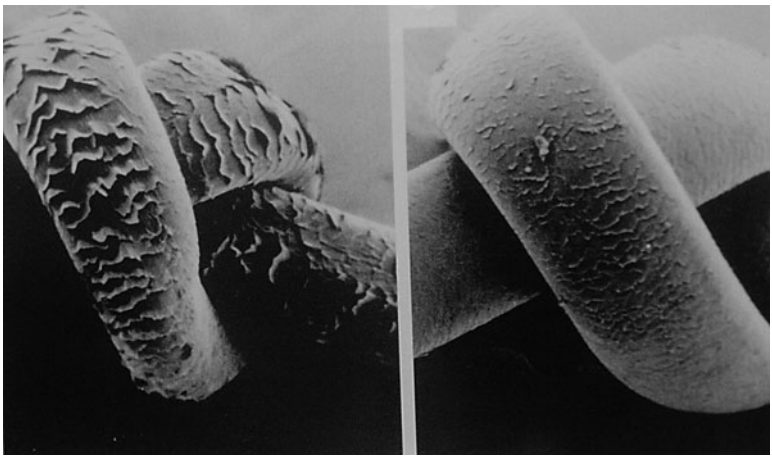

Fig. 9.39 Both hair fibers extension cycled 200 times to 20% extension at 10% RH and put into water and knotted by Gamez-Garcia [16]. *Right*: Fiber treated with 3% cystine polysiloxane prior to knotting. *Left*: Control fiber. Note the lack of scale lifting from the polysiloxane treated fiber (reprinted with permission of the Journal of Cosmetic Science)

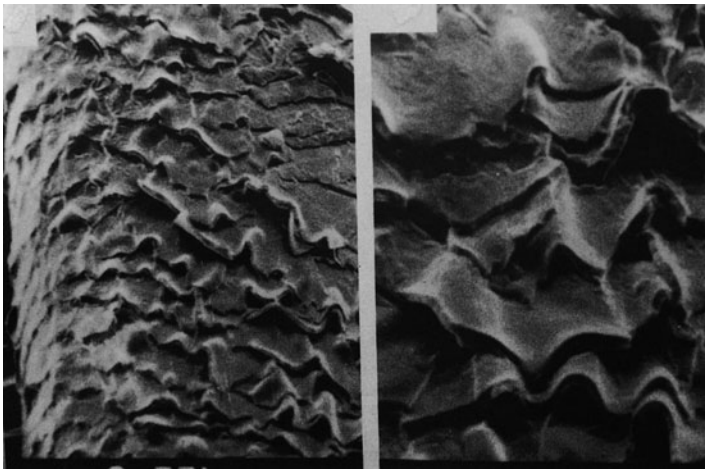

Fig. 9.40 Hair fiber extension cycled to provide scale lifting then treated with 3% polyethylene imine and then three cycles of wetting and blow drying by Gamez-Garcia [16]. Note the severe scale lifting and folding caused by this polymer treatment (Reprinted with permission of the Journal of Cosmetic Science)

Inhibition or promotion of scale lifting and hair fragmentation by isolated polymers or ingredients can be informative in terms of helping to explain the mechanism of fiber degradation from stretching, bending, torsion and abrasive actions. However, such treatments are often of limited use in product formulation

studies, because the addition of other ingredients to make a finished and aesthetic formulation often changes the nature and effects of the active ingredient on cuticle fragmentation or protein loss. For example, hair fibers with a weakened cell membrane complex from permanent waving and stretching when treated alternately with triethanol ammonium lauryl sulfate and stearalkonium chloride produced pronounced scale lifting and distortion. On the other hand, the addition of cetyl alcohol (a common additive in crème rinses) to the stearalkonium chloride produces noticeably less scale lifting and distortion.

Certain shampoo formulations with cationic guar produce scale lifting. However, other formulations with only small formula changes produce no detectable lifting or less protein loss. Thus the combination of ingredients in a formulation can either retard penetration and/or deposition into the cuticle or alter the interactions of an active ingredient with functional groups that are a part of the structure of hair and change the effects on cuticle/hair damage.

Hair fibers with a weakened cell membrane complex/endocuticle are exceedingly sensitive to penetrating ingredients. Ingredients that penetrate into these regions can either remove or breakdown non-keratin components or can deposit and promote cuticle lifting and scale distortion. On the other hand, those penetrating ingredients that diffuse into the cell membrane complex-endocuticle and interact by bonding so as to either plasticize or provide adhesive bridges to the weakened layers can strengthen the cuticle and make it more resistant to fragmentation and protein loss. Furthermore, scale lifting methodology (extension cycling or fatiguing evaluated by microscopy and/or light scattering) is more effective for distinguishing between these types of damage and repair than tensile or load-elongation methods which have not been shown to be capable of detecting changes in the cuticle.

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Chapter 10
Definitions of Consumer Relevant Hair Assembly Properties and How These are Controlled by Single Fiber Properties

Abstract Herein is an attempt to bridge the gap between consumer and scientist by defining the more important consumer hair assembly properties (heads of hair, tresses, or wigs) describing how these properties are affected by changes from cosmetic treatments to fundamental single fiber properties. The effects of changes in single fiber properties by chronological age for five different stages of one's life is also described in terms of how these fiber properties relate to and affect the important consumer hair assembly properties. The literature on hair breakage is also summarized as a multifactorial phenomenon involving tangle formation with hairs looped over other hairs, severe bending deformations, highly localized stresses, and the amount of water in the fibers. The effects of hair curvature, fiber twists, knots, hair damage and abrasive wear on hair breakage are also described. A new unpublished section describing split hairs found on the heads of consumers is described along with preferred mechanisms for the formation of these different types of split hairs.

10.1 Introduction

This new Chapter defines and summarizes the literature on the more important cosmetic hair assembly properties (CHAP) of human hair including, hair conditioning, hair strength, hair breakage, split ends, flyaway hair, luster or shine, combing ease, hair body, style retention, manageability and hair handle or feel. Hair feel assessments include dryness-oiliness, clean-feel, conditioned-feel, softness and smoothness, etc. are important assessments that are currently being addressed and is summarized in the section entitled *Hair Handle or Feel*.

Over the past several years these elusive cosmetic terms, hair conditioning, hair damage, hair strength, hair body, manageability and moisturization have been defined in ways that have permitted progress to be made in terms of understanding these properties and in stimulating new methods for their measurement. Therefore,

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I decided to define these and other important CHAP all together in this Chapter. Some of these definitions are new; however, several have been taken or slightly modified from the cosmetic literature including the following references [1–7] and sections of Chap. 8 in previous editions.

This Chapter also contains a summary of the hair literature on hair breakage and some new information on the splitting of hairs that actually occurs on live heads. This information shows that splitting of hairs is accelerated by cosmetic treatments and sunlight exposure that involve free radical reactions on the cortex cell membrane complex of hair.

Some of the more important cosmetic terms are defined below including:

Combing ease: the ease of aligning hair fibers of a tress or hair assembly with a comb so the fibers are essentially parallel [1, 2].

Frizziness: when the curvature of neighboring hairs of an assembly are not synchronized (parallel) producing the appearance of disorder or disarray near the ends [3].

Hair body: is primarily the apparent volume of an assembly of hair fibers [1], but it is defined in more detail on the next few pages.

Relative scalp coverage or "Amount of Hair": a new metric for the manner in which hair provides coverage to the scalp [7].

Style retention: the ability of an assembly of hair fibers to retain a style that it is placed in for several hours after grooming (time limit is arbitrary, but longer than grooming operations) [1].

Manageability: the ease of putting hair into place and its temporary ability to remain in place during styling operations. See additional details below [4].

Flyaway hair: the static ballooning of a hair assembly at a specific RH by controlled combing, brushing[1] or rubbing.

Luster: a scientific term to measure consumers' assessment of hair shine.

Hair breakage: is only relevant as it relates to and explains breakage that occurs on the head of consumers. The most relevant tests for breakage are those that count or weigh the hairs that are broken in hair combing or brushing tests or those that correlate closely with that type of test.

In addition to the definitions above, definitions for Hair Conditioning, Hair damage, Hair Strength, Hair Body, Moisturization and additional details for Manageability are provided below:

A good working definition for **Hair Conditioning** is based on the action or function expected by consumers for this type of product. Thus, a hair conditioner is an ingredient or a product, that when applied to hair in its recommended use procedure and concentration improves the combability relative to appropriate controls. For testing an ingredient in a product, the control should be a product containing all ingredients except the potential active. In the case of a product, the control should be a cleansing medium such as 12% sodium lauryl sulfate or sodium laureth-2 sulfate in water.

This definition does not say that combability is the only property of a hair conditioner, but it defines combability as the "acid test" or the "price of entry"

for a hair conditioner. Different combing tests to assess hair conditioning are described in the section entitled, *Combing Ease*. Market research studies with consumers and current scientific literature are consistent with the above definition. The advantage of this definition is that it permits ease of combing a method that can be used for reproducible measurement to be used to study and to improve hair products for conditioning.

Hair Damage is defined and described in detail in Chap. 6 in the section entitled, *Damage to Hair from Shampoos, Grooming and Weathering*. **Hair Strength** may be defined as the ability to resist hair breakage by grooming actions and is defined further in the section entitled, *Breakage of Hair during Grooming Actions* in this Chapter. Methods to assess these important properties are also described in these same sections.

Hair Body has been defined by Robbins [1] as thickness or apparent volume of a hair assembly, involving sight and touch for assessment. This definition does not lend itself to one simple method for measurement, however, it does help to improve our understanding of this important hair property and it has permitted several scientific tests to be proposed that correlate with hair body. For a more complete discussion on the utility of this definition, see the section on *Hair Body* in this Chapter.

Manageability [4] involves the ease of arranging hair in place and its temporary ability to stay in place during the grooming process; that is while arranging hair in place. Long-term effects on hair behavior (after one is finished arranging the hair in place) are actually style retention and not manageability. Manageability is an even more complex consumer assessment than hair body. It is such an inclusive term that it cannot be measured by one single procedure. Robbins et al. [4] recommended considering this important cosmetic property in terms of its component fiber assembly properties, such as different types of manageability that can be more readily visualized and measured. Manageability is concerned with:

Arranging hair in place (combing/brushing),
Keeping hair in place (style retention during styling), and
Flyaway hair.

Therefore, the suggestion was made [4] to consider these three types of manageability to permit measurement and scientific evaluation, rather than the single elusive term manageability. The section on manageability (later in this chapter) explains how to prioritize and use methods relevant to these three types of manageability.

Moisturization of hair is another important cosmetic term that has been misunderstood in the past. Because this word is derived from moisture, some jump to the conclusion that moisturization should relate to the water content of the fibers. Actually moisture in hair is a scientific or technical term determined by the amount or percentage of water in hair and it can be measured, see the section in Chap. 9 entitled, "*Water (RH), pH and Solvents and the Dimensions of Hair*". On the other hand, moisturization is a consumer (ist) term not a scientific term. Davis and Stofel [5] described the consumers' perception of moisturized hair vs. the actual water

content. These scientists [5] demonstrated that the consumers' perception of moisturized hair does not correlate positively with the amount of water in hair, but it does correlate with consumers' perception of smoothness of hair. For example, trained panelists were asked to rate hair tresses for moisturized hair equilibrated at 15% RH vs. the same type tresses at 80% RH when the tresses were brought together rapidly at 45% RH. The hair tresses that had been equilibrated at 80% RH were judged to be less moisturized even though they were found to contain higher water content at the time of evaluation. The apparent discrepancy here is that the hair with the higher water content has a higher friction coefficient and feels rougher.

These scientists also asked panelists to rate shampooed hair vs. hair treated with shampoo plus conditioner for% moisturization. The conditioner treated hair was judged as more moisturized by a large margin even though the samples had identical water content at the time of evaluation. Additional related experiments were run demonstrating conclusively that the consumers' perception of moisturization is not at all related to the water content of the hair but to smoothness and softness. Therefore, the hair feel involving smoothness or fiber friction is clearly a more reliable estimate of the consumers' perception of moisturization or moisturized hair than the actual water content of the fibers.

The above definitions of hair conditioning, hair damage, hair strength, hair body, manageability and moisturization, in all cases, do not provide a single method to measure these properties; however, they do permit a better understanding between scientist and consumer and a better overall understanding of these important consumer hair assembly properties. Therefore, these definitions will permit science to move forward to improve these important hair properties for consumers.

10.2 Combing Ease

As indicated earlier, combing ease may be defined as the ease of aligning fibers of an assembly with a comb so that they are essentially or more parallel. Combing ease may be considered in terms of a combination of single-fiber properties or treated as an assembly property. Robbins and Reich [2] conducted a very large study relating quantitative combing behavior to the single-fiber properties of curvature, friction, stiffness, and diameter for straight, wavy, and very curly hair. These different hair types were each treated with a shampoo detergent (sodium lauryl sulfate), a long-chain quaternary ammonium compound (stearalkonium chloride), a commercial pomade (from mineral oil and petrolatum), and a hair bleach (peroxide/persulfate system).

In their analysis of combing ease, Robbins and Reich [2] demonstrated that combing forces can be quantitatively defined by the square of the fiber curvature while considering only linear terms for friction and fiber stiffness as in this equation for 3 g tresses of 10 in. hair:

$$\log PCL = 0.0057\ C^2 + 1.48\ F - 0.05\ S + 1.66$$

PCL = Peak combing load; C = curvature; F = friction; S = stiffness

$r^2 = 0.96;\ p<0.0001$

Fiber diameter did not provide a significant contribution to combing forces (because diameter correlates with stiffness). Fiber friction was determined by a capstan method measuring friction of hair fibers over a hard rubber mandrel at a high load of 1 g per fiber [2].

The above quantitative combing expression suggests that when hair is curly to highly coiled as for curly African American hair or hair permanent waved on small rollers, curvature tends to dominate combing behavior and changes in friction and stiffness play only a minor role leading to the C^2 hypothesis of Robbins. However, when curvature is low as for wavy to straight hair of all types, for example, Curl types I, II and III (by the STAM system, see Chap. 9) such as most Caucasian or Asian hair or even wavy to straightened African hair, friction plays the major role with only a small contribution from fiber stiffness. This conclusion was confirmed by regression analysis of the data for only wavy and straight hair showing that curvature effects are not significant with hair of low curvature as in average Asian or Caucasian hair or straightened African American hair.

In an unpublished part of this same project naturally curly African American hair from several female panelists was examined. This hair was cut directly at the scalp, and tresses were made from it. Its combing behavior compared to the combing behavior of curly to highly coiled steam set Caucasian hair (two different lots of differing curvatures). Both types of hair were reasonably close to the combing values predicted by a combing equation involving the square of the fiber curvature.

The results of this latter study are in agreement with what is essentially the reverse experiment by Epps and Wolfram [8]. These scientists concluded that, "straightening of Black hair whether by chemical (relaxers) or physical (hot combing), results in hair whose assembly behavior is indistinguishable from Caucasian hair". Robbins actually straightened some of the naturally curly African American hair using a commercial alkaline straightener and confirmed that the combing forces for hair tresses from this hair were similar to that of tresses made from wavy Caucasian hair and in agreement with values predicted by a combing equation.

The work from these two different laboratories confirms that using very curly highly elliptical hair from African Americans (ellipticity = 1.76) and very curly hair of Caucasians of low ellipticity (ellipticity = 1.38) that the longitudinal shape (hair fiber curvature or curliness) is the primary factor governing combing forces and not the elliptical cross-sectional shape of the fibers.

Robbins and Reich also demonstrated that the primary reason the combing forces are lower for wet curly hair vs. dry curly hair is an effect on fiber curvature. Wetting out the hair in a tress or an assembly actually uncurls the fibers to some degree decreasing the fiber curvature. This water straightening in high curvature hair is sufficient to provide a significant decrease in combing forces in agreement with the values found by quantitative combing.

Table 10.1 How single fiber properties relate to combing ease [2]

Increase in these fiber properties makes combing easier	Increase in these fiber properties makes combing more difficult
Stiffness	Curvature[a]
Diameter[b]	Friction
Cohesion	Length
	Static charge (chargeability)[c]

Note: Fiber length is not changed by cosmetic treatments
[a]A relatively large effect, and the effect increases with increasing curliness
[b]Relatively small effect
[c]A relatively small effect is predicted

Table 10.1 describes how "changes" in the more important fiber properties affect combing ease. This table suggests that increasing fiber curvature, friction or static charge will each make hair more difficult to comb. Fiber length cannot be changed by cosmetic treatments. On the other hand, increasing fiber stiffness, diameter, or cohesive forces will make hair easier to comb as confirmed by the study of Robbins and Reich [2].

Table 10.1 indicates that curvature has the most impact on combing forces. When the curvature changes are relatively small and the fibers are straight to wavy, the curvature effect on combing forces is small, but at higher curvatures the effect on combing forces increases until it becomes dominant. Fiber friction and stiffness also contribute to combing behavior. The effect of these two variables becomes more important as curvature decreases and they are most important when the hair is relatively straight. Fiber diameter was not significant in the quantitative study by Robbins and Reich [2] because it is collinear with and contained in stiffness.

Increasing fiber curvature or fiber friction makes combing more difficult as expected (see Table 10.1). However, increasing fiber stiffness results in lower combing forces. Pomades and other oily or wax-containing conditioning products are used in leave on products and large amounts of these materials, are left on the hair surface. These low level cohesive forces serve to lower combing loads. This effect occurs because these ingredients' inhibit the reformation of entanglements as the comb traverses through the hair. Thus, cohesive ingredients facilitate combing by helping to keep the fibers more parallel.

10.2.1 Methods to Evaluate Combing Ease

Qualitative combing of tresses in replicate and evaluation of the data by nonparametric statistics can be a powerful tool when properly applied. This procedure provides a fast, sensitive, and reproducible method for the development of products. However, quantitative instrumental methods have also been useful [9–12]. Basically, these methods consist of attaching a tress or swatch of hair to a strain gauge such as the load cell of an Instron tensile tester and measuring the forces and/or work required to move a comb through the tress under controlled conditions.

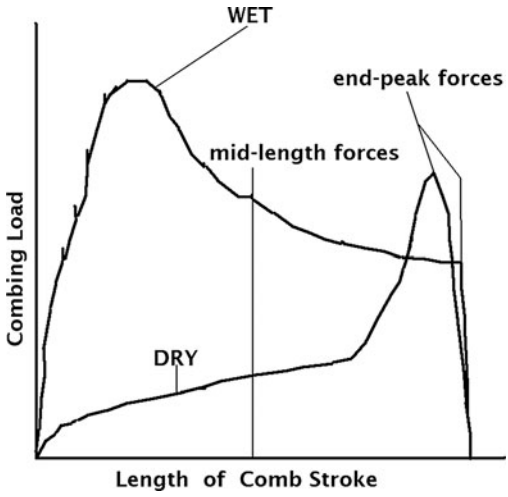

Fig. 10.1 Schematic of wet and dry combing force curves for hair from tresses of low curvature Caucasian hair (curl type II)

Figure 10.1 represents a schematic of typical wet and dry combing force curves for a single comb system with relatively straight hair such as Curl types I, II or III. Note the high end peak force for the dry combing vs. the wet combing and the relatively high mid-length force for wet vs. dry combing. Analysis of combing force curves tells us that dry combing reveals tip end conditioning, and tip damage, along with short segment breakage better than wet combing. However, wet combing is better for revealing longer segment breakage and conditioning over the mid-length portion of the fiber.

Figure 10.2 represents a schematic of typical dry combing force curves for very curly hair; for example, Curl type VI or higher vs. relatively straight hair, such as Curl type I or II. Note the extremely large differences in the relative combing forces. The curves for Fig. 10.2 were drawn to represent combing forces where the same type comb is used with both hair types. In practice, this would not be the case because the person with Curl type VI or higher will use a comb with wider spaces between the teeth or a pick.

An interesting modified version of this test is the one by Kamath and Weigmann [12] that involved a double comb system wherein the combs are about 100 mm apart. With this system, the first comb helps to remove snags while the second comb measures the hair on hair plus hair on comb rubbing forces. Figure 10.3 is a schematic representing the combing forces for a double comb system. In a single or double comb system, the mid-length combing loads or the forces or work of combing (total area under the curve) are related to long segment breakage. On the other hand, the end peak force is related more to short segment breakage.

An alternative approach to the determination of combing forces is the raspiness method of Waggoner and Scott [11]. This method utilized an electronic comb designed to pick up vibration frequencies emitted as the comb teeth rub along the hair scales.

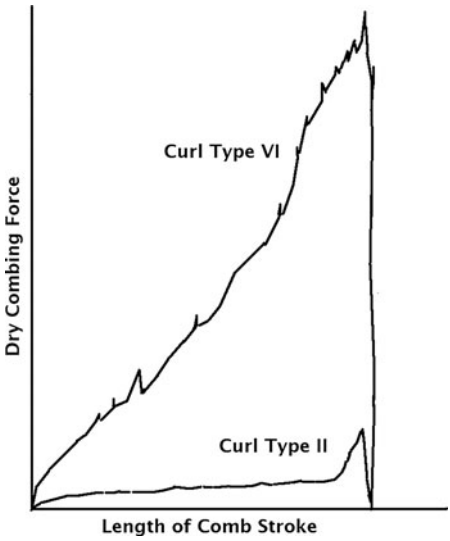

Fig. 10.2 Schematic of dry combing force curves for a hair tress of low curl (curl type II) compared with a hair switch made of high curvature hair (curl type VI)

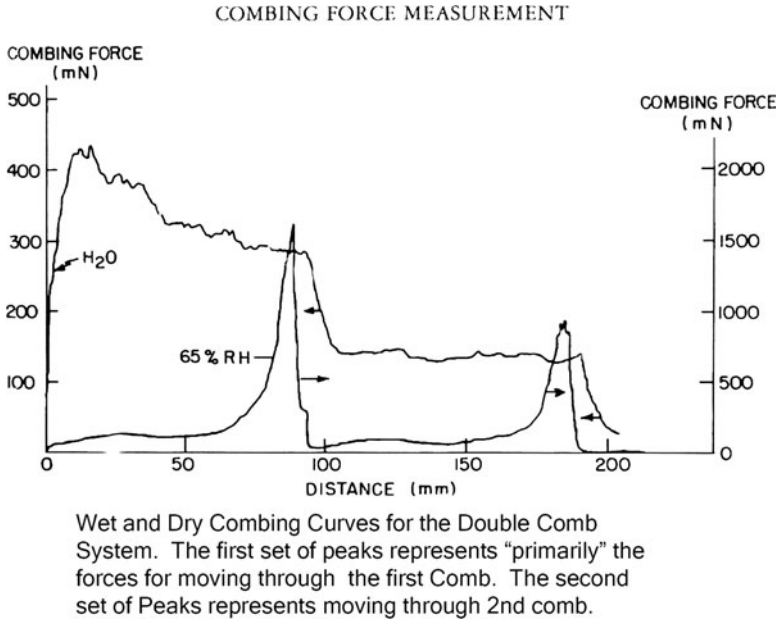

Fig. 10.3 Schematic of wet and dry combing force curves for the double comb system of Kamath and Weigmann [12] for Caucasian hair of low curvature (Reprinted with permission of the Journal of Cosmetic Science)

10.2.2 Treatment Effects on Combing Ease

Both permanent waving and bleaching make hair more difficult to comb [2, 10]. Permanent waving increases both fiber curvature and inter-fiber friction [2], primary factors that make hair more difficult to comb (see Table 10.1).

In the case of bleaching, the primary factor is the friction increase [2, 13]. There is no measurable curvature change in bleaching [2]. Stiffness [2] and diameter [2] changes are also negligible from bleaching. In contrast to permanent waves and bleaches, conditioners [9, 10, 13] and some conditioner sets make hair comb easier by providing a decrease in inter-fiber friction. Chargeability [13, 14] may also decrease, thus helping to improve dry combing. Pomades decrease fiber friction and increase low-level cohesive forces between hairs. This cohesive effect helps to inhibit the formation of entanglements beneath the comb as it travels through the hair. At the same time it helps to keep the fibers parallel after each comb stroke. Thus, cohesive forces from oily ingredients make hair comb easier.

Shampoos are a category with wide variability because these products can make hair either easier or more difficult to comb (Ross, private communication). High-cleaning shampoos with anionic surfactants remove surface oils, increasing inter-fiber friction (Chap. 9) and thereby make clean hair more difficult to comb than greasy hair. However, certain conditioning shampoos deposit ingredients onto the hair surface and decrease fiber friction, making hair easier to comb.

Shampoo ingredients [13, 14] can also alter the chargeability of the hair. For example, high-cleaning shampoos remove surface oils and deposit small amounts of anionic surfactant onto the hair, thus increasing chargeability. On the other hand, some conditioning shampoos lubricate the hair surface, providing easier combing and at the same time decreasing chargeability, leading to less flyaway and easier dry combing. Other conditioning shampoos deposit conditioners that improve wet combing, but they increase flyaway hair demonstrating that the nature of the deposit is critical to chargeability and to static charge. Changes in fiber stiffness, curvature, and diameter by current shampoos are negligible. Therefore, changes in these properties are not relevant to combing effects by current shampoos.

10.3 Breakage of Hair During Grooming Actions

Research shows that methods such as combing hair and collecting the broken fragments and either counting or weighing the broken hairs [15–20] is the best approach to measuring or estimating hair strength. Abrasion to break [17] which has also been called flex-abrasion by Leroy et al. [18] and impact loading [19] are more relevant than tensile testing to hair breakage during grooming because they relate

more to the actual strength of hair fibers under the stresses of abrasion, bending and/or impact actions. These methods will be considered in this section.

Abrasion resistance and the resistance to break under abrasive stresses (flex-abrasion) are methods that should receive more attention in the future because of their closer relationship to some, but not all of the stresses that actually damage hair and ultimately lead to hair breakage during grooming actions. The apparatus built by Textile Research Institute of Princeton, NJ under the guidance of Sandhu and Robbins [17] illustrates this type of test procedure, see Fig. 10.4. Rubbing hair fibers to break on this apparatus is capable of differentiating between some conditioning shampoos.

Furthermore, work by Swift et al. [20] suggested improvement in the sensitivity of this method beyond this earlier work. This system merits further investigation, because of the relevance of rubbing, bending and compressive actions to everyday hair grooming/hair wear and fiber breakage. The protein loss method measures cuticle and cortical fragmentation damage and is a measure of abrasion resistance and dissolution; however, it is not a measure of catastrophic failure of hair fibers.

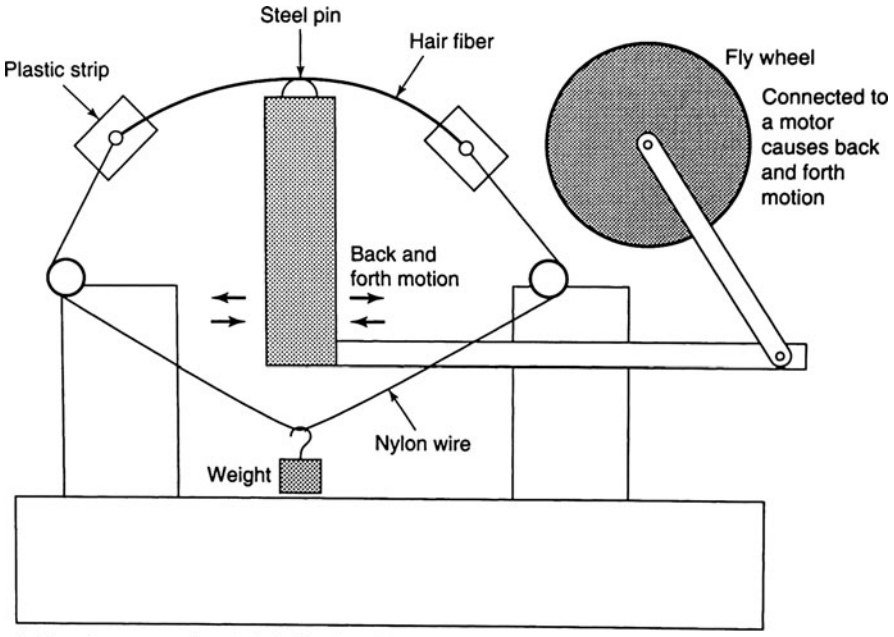

Fig. 10.4 Schematic illustrating an instrument developed by TRI Princeton and S. Sandhu to study abrasion to break

10.3.1 Evidence that Hairs Don't Break from Tensile Elongation by Combing or Brushing

There are several important papers in the scientific literature on the fracturing and breakage of human hair fibers [15, 19–29]. However, there is relevant literature that raises questions as to how relevant tensile test conditions are for simulating or for predicting hair breakage on live heads [21, 22, 25, 28, 29] or from combing or brushing human hair tresses in the laboratory.

Contrary to a superficial assessment, most hair fiber breakage that occurs during combing or brushing does not result from simple tensile elongation. Hamburger, Morgan and Platt in 1950 [21] demonstrated that the load to pull Caucasian hairs out of the scalp was about 45% of the load required to break hair fibers at 65% RH. Subsequently, Berthiaume et al. [22] published results that the pullout load for Caucasian hair is about 40–45 g (slightly higher than that of Hamburger et al. [21]), for African hair 30–35 g and for Asian hair 60–65 g. Back calculating the average load to break at 65% RH from the breaking stress for these three different types of hair provides breaking loads for average Caucasian hair at about 76 g, for average African hair at 73 g, while average Asian hair should be more than 100 g because of its larger area of cross-section. Therefore hairs must be damaged extensively or they will pull out before breaking by tensile elongation; however, an alternative is that hairs must break by another mechanism.

An equally important factor to consider is the percentage extension to break for hair fibers at 65% RH which is about 50% for Caucasian and Asian hair and about 40% for African type hair at 65% RH (discounting premature failure) and even greater at higher humidity. Hair on the head just does not stretch to this extent before breaking.

10.3.2 Hair Fibers Bend and Loop Around Other Hairs Forming Tangles Which Break Hairs by High Localized Forces from Pulling a Comb or Brush Through a Tangle

Combing and brushing hair of Curl types I–III (by the STAM procedure) have been studied more systematically than higher Curl types and have been shown to provide two types of breakage, short segment breaks (less than 2.54 cm) and longer segment breaks. Brown and Swift [29] examined the arrangements of hair fibers in snags while combing tresses in a scanning electron microscope to try to understand more fully how hair fibers break during combing. These scientists concluded that hair fibers loop over other hairs (see Fig. 10.5) and that hair on hair interactions with severe bending actions are involved in hair breakage during grooming.

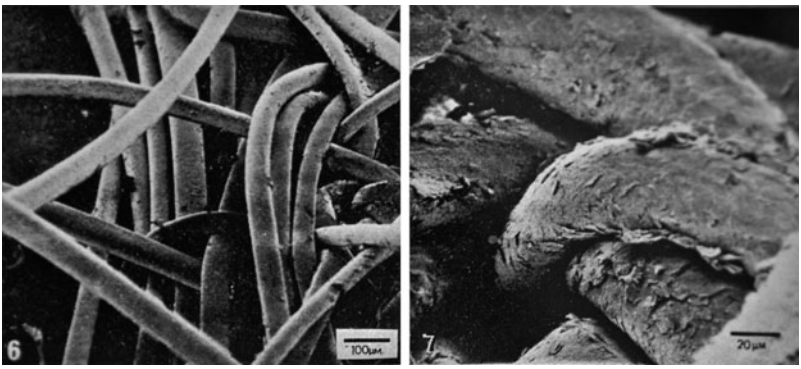

Fig. 10.5 Small tress combed in the SEM showing hairs looped around other hairs by Brown and Swift [29] (Reprinted with permission of the Journal of the Society of Cosmetic Chemists)

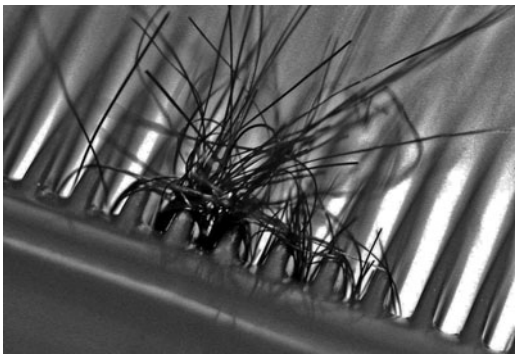

Fig. 10.6 Hairs wrapped around comb teeth and other hairs in a snag [27] (Reprinted with permission of the Journal of the Society of Cosmetic Chemists)

Robbins [19, 26] studied hair breakage by combing hair tresses and examining photographs of snags of hair fibers in combs. The resultant hair fiber arrangements provided support to the evidence and the conclusions of Brown and Swift that breakage involves hair on hair interactions (see Fig. 10.6) where hairs loop and bend over comb teeth and over other hairs to provide sites for hair on hair breakage through highly localized forces on impact while pulling through a tangle. Furthermore, in combing experiments broken fragment size related to the site of higher combing forces in combing force curves suggesting that breakage occurs primarily at or near the hair to comb interface.

Even though these experiments were on Curl types I–III, it is likely that Curl types IV–VIII break similarly because the more highly coiled the hair the more looping and entanglements and higher combing forces and as we shall see breakage increases with combing forces. In addition, Robbins and Kamath [28] demonstrated an increase in breakage with hair fiber curvature corresponding to higher combing forces with higher curvature.

Fig. 10.7 Ends of hair fibers wrapped around comb teeth in a snag [28] (Reprinted with permission of the Journal of the Society of Cosmetic Chemists)

10.3.3 Hair Fibers by Combing or Brushing Break into Short and Longer Segments

Evidence suggests that longer segment breaks (generally longer than 2.54 cm) occur primarily by one hair fiber bending over or wrapping around another hair (as illustrated in Fig. 10.6) and impact loading [19]. Furthermore, breakage by bending and impact loading occurs at a hair to hair contact point with essentially no increase in hair length (strain) as compared to normal tensile loading which requires large strain increases [19, 28–30]. On the other hand, short segment breaks (less than 2.54 cm) involve end wrapping of the distal ends of hairs about comb teeth or brush bristles [19, 26–28], see Fig. 10.7. This action at the fiber ends (especially in the dry state) increases the end peak force and with continued abrasive damage to the ends produces an increasing number of short segment breaks [26–28]. The formation of entanglements is a critical determinant for both long and short segment breaks including hair on hair and hair on comb entanglements and abrasion is more important to short segment breaks than long segment breaks.

10.3.4 Hair Breakage Increases with Hair Fiber Curvature

Combing forces increase with the second power of hair fiber curvature as shown by Robbins and Reich [2]. The middle portion of the combing curve and the work of combing relate more to long segment breaks, while the end peak force relates more to short segment breaks.

Robbins and Kamath [28] compared the number of short and long segment breaks by combing hair tresses that had been permanent waved into Curl type II and Curl type III configurations. These scientists found large increases in both the number of short and long segment breaks with increasing curvature. The increase in

the long segment breaks are due to more snags that occur from entanglements higher up in the tress produced by higher curvature. Even though the number of long and short segment breaks increased with curvature, the number of long segment breaks increased more than the number of short breaks.

The effect of hair fiber curvature on fiber breakage is well known among consumers, because grooming devices were developed centuries ago to help compensate for curvature effects. For example, combs with small teeth and narrow spacing are normally used for short straight hair, while combs with larger teeth and wider spacing are normally used for hair of medium curvature. On the other hand, combs with very wide spacing called picks are used with hair of high curvature such as Curl types V through VIII or even for some persons with Curl type IV.

10.3.5 Curly Hair Forms Knots Which Also Break on Impact at the Site of the Knot

Khumalo et al. [31] examined a large number of broken and pulled out hair fibers from two Africans (from South Africa). This hair was most likely one of the higher Curl types between V and VIII. Two Asian and two Caucasian volunteers were also on this panel. These panelists had never used chemical treatments on their hair. The volunteers shampooed and combed their hair (using their usual combs or picks) for 4 days in a row and collected the hairs each day from the combings. At the beginning of the experiment, the average hair length of the African hair was 5 cm, for the Caucasians 22 cm and for the Asians 25 cm. Since the two Africans had not cut their hair for more than 1 year and since the growth rate is about 13 cm per year, these facts testify to the high rate of breakage from high stresses, the fragility and the deformations imposed on highly coiled African hair by grooming actions.

The total number of hairs collected was, 1,163 from the Africans, 464 from the Caucasians and 200 from the Asians. Random samples of 100 hairs (or the total number of hairs) from each person for each day were examined visually, by light microscopy and by SEM. For the Africans, 35% of the hairs had bulbs. Therefore, these hairs were pulled out of the scalp by grooming actions leaving 65% broken hairs. For the Caucasians, 85% of the hairs were pulled out and 15% broken. Ninety two percent of the hairs from the Asians were pulled out, providing only 8% broken hairs from the Asians. These scientists also observed that 13.3% of the African hairs examined had knots. This average was relatively consistent each day providing 106 knots in 800 hairs over the 4 day period. This knot formation contrasted to only one knot found in the hair of 464 Caucasian hairs and no knots in 200 Asian hairs.

These scientists proposed that knot formation in the highly coiled African hair is involved in breakage of some curly to highly coiled hairs. Robbins [26] demonstrated that hairs in a knot under light impact loads break much more readily

than unknotted hairs and the break forms at the knot. The severe bending in the knot produces extensive elongation and compression over a very short segment of the fiber making it more susceptible to breaking. These results confirm once again the importance of bending actions to hair breakage described by Swift and Brown [29]. So, highly coiled hair fibers such as Curl types IV–VIII tend to form knots and many break through this mechanism [19, 31]. And, the more highly coiled the hair the higher the propensity for knot formation. So, some curly hairs do form knots and break by impact at the site of the knot, however, knots generally account for a small percentage (probably a maximum of about 13–26%) of the broken hairs.

10.3.6 Hair Chemically or Physically Damaged Breaks Easier than Non-Damaged Hair

Chemical damage by perms (Chap. 4), bleaches (Chap. 5), permanent dyes Chap. 5 [32], straighteners (Chap. 4) [33] and sunlight exposure (Chap. 5) [34] weaken hair and increase inter-fiber friction leading to more tangle formation and more breakage. On the other hand, hair conditioners make hair comb and brush easier and have been shown to produce less breakage [27] (see Table 10.3 in Section 10.4.2 entitled Causes of Split Hairs and Split Ends).

Relative humidity or the amount of water in the fibers also affects combing forces and hair breakage [27]. Epps and Wolfram [8] demonstrated that the work of combing of highly coiled African hair is lower wet than dry, but the reverse holds for wavy to straight Caucasians hair where the combing forces are higher wet than dry [27, 35].

Physical damage or wear by abrasion [22, 27] occurs from grooming devices such as combs, picks or brushes and to some extent a fatiguing action. Wear by abrasion occurs over the entire fiber but more near the fiber tip ends because of a longer residence time, but even more so by high end peak forces when combing or brushing hair dry [22] as evidenced by examination of many of the smaller fragments of short segment breaks [22, 27].

10.3.7 Hair Fibers with Twists Contain Flaws and Can Break Prematurely

As indicated earlier, the work of Kamath, Hornby and Weigmann [24] showed "premature failure" (breakage occurring at 20% extension or less) on 22% of the hair fibers from one African American male. In addition, 17% of the fibers broke within 8% extension at 65% RH. These scientists concluded that premature failure generally occurred in a region of twist. Interestingly, premature failure virtually disappeared when the African American fibers were wet with only about 2%

breakage within 33% extension [24]. So, premature failure for African type hair is primarily a dry state phenomenon.

This particular African hair examined by Kamath et al. [24] had a very high ellipticity (1.89) suggesting it is of Curl type VII–VIII. In addition, the load to break for this type of hair in the 3–20% strain area (the yield region) would be one-half or less of the average load to break at 65% RH and very close to the pull out load. Nevertheless, it is still likely that this type of hair breaks more frequently from bending than stretching stresses as suggested by Brown and Swift [29], that is, it would more likely break by bending and impacting over another hair [19, 26–28] or by severe bending and deformation in a knot [18, 31] rather than by tensile loading. In a few instances it is possible that tensile breakage could occur with this type of hair. The wet breaking stress is lower for curly hair, therefore, dry breakage for highly coiled African type hair should be more severe than wet breakage because of the higher grooming forces in the dry state [2, 35]. The fact that premature failure occurs in the dry state and it is virtually eliminated in the wet state and the fibers are more extensible when wet [36] are other reasons favoring dry state breakage for highly coiled hair.

10.3.8 Hair Breakage Correlates with Combing and Brushing Forces and the Location of the Break on the Fiber Corresponds to Where the Higher Combing Forces Occur

Accumulated data from conditioned vs. shampooed hair [27], bleached vs. unbleached Caucasian hair [27] and comb stroke length comparing broken hairs vs. combing loads (Crawford, private communication) shows that hair breakage increases with combing forces. Pearsons's non-parametric correlation test of these data provides a significant correlation for this effect. Furthermore, Kamath and Weigmann [12] observed that wetting and combing Caucasian hair tresses provides a large increase in the mid-length force and at the same time a decrease in the end peak force compared with combing hair dry (65% RH). A few years later, Robbins and Kamath [27] observed more short segment breaks in dry vs. wet combing for Caucasian hair, but more long segment breaks in wet combing. Furthermore, we have shown in our own laboratories that cross cutting hair and combing it dry vs. a tapered cut provides even higher end peak forces and more short segment breaks (see Table 10.4 in section 10.4.2 entitled Causes of split hairs and split ends). These results confirm that combing forces correlate with hair breakage but more importantly the location on the fiber where breaks occur during combing actually corresponds to where higher combing forces occur in combing force curves. In other words, mid-length combing forces correspond to long segment breakage and the end peak force corresponds to short segment breakage. This relationship suggests that hairs break near the hair to comb interface in tangles.

10.3.9 Fatiguing and Hair Breakage

Evans and Park [37] suggested that fatiguing is the primary reason for hair breakage. On the other hand, Kamath and Robbins [15] considered the prior literature on hair breakage and suggested that hair breakage is a multifactorial phenomenon as described above involving looping, bending and breakage by highly localized stresses generated from impact during combing or brushing through a tangle.

Fatiguing occurs primarily between the root section of the fiber and the brush or comb when the combing device encounters a snag, but only on the fibers under tension in that snag and when the same fibers are under tension on thousands of repeat cycles because low cycle fatiguing is defined as less than 50,000 cycles. If we consider fatiguing as two to millions of cycles of highly variable stresses then it covers virtually every event. But, thousands of fatiguing cycles in exactly the same spot on the same fiber happens to only a low percentage of the fibers in the comb or the brush. So, fatiguing is a lower probability process than for a single hair under high tension to be impacted once or even a few times and broken. It is likely that in many cases hairs are damaged or even weakened by a fatiguing action (especially near the tips), however in most cases catastrophic failure occurs from a high localized impact of one hair bent over another in the damaged or undamaged region of the fiber.

Evans and Park [203] used Weibull statistics to calculate the shape parameter and the characteristic life for virgin and bleach damaged hair, and hair treated with conditioners. The definition of the characteristic life for hair breakage in their experiment is the number of brush strokes necessary to break 63.2% of the fibers. For virgin hair, the characteristic life is 55.2 million brush strokes. But, for the same hair after conditioning it increases to 1.04 billion brush strokes. But the data for these huge numbers are based on only 10,000 brush strokes when only 1.6% of the fibers broke (326 of 20,000) as compared to 12,640 fibers corresponding to their definition of characteristic life. These characteristic life values are so large relative to the actual data that they are of questionable reliability. For additional concerns about the application of Weibull statistics to hair breakage data, see the paper by Kamath and Robbins [15].

Therefore, the fracture mechanism based on flaw propagation by fatiguing in real brushing and combing situations requires thousands of cycles. So, fatiguing actions on the same region of the same fiber may occur with a few fibers, but it cannot be the primary cause of hair breakage especially for long segment breaks as shown above and in the following section.

10.3.10 Where Hair Fibers Break Favors a Mechanism Involving High Localized Stresses

Where hair fibers break (along the length of each fiber) during combing and brushing corresponds very closely to the higher combing forces in combing force

curves as described above. This fact supports the mechanism of Robbins and Kamath [15] that involves high localized stresses and a few impacts rather than thousands of cyclic stresses for the fatigue mechanism of Evans and Park [37].

In the fatiguing process (primarily in the elastic and/or plastic regions) a crack is likely to initiate anywhere between the snag and the root section of the fiber, but not primarily near the same location and in fatiguing the snag must always be at the same spot on the same hairs. Furthermore, once initiated, the crack is propagated and terminated by thousands of fatiguing actions at exactly the same spot. Therefore, fatiguing would not be expected to show such a close relationship between the location on the fiber where catastrophic failure occurs and the hair to comb interface in tangles as has been found.

This rationale holds especially for long segment breaks. Some short segment breaks likely involve a fatiguing action, but even most short segment breaks will ultimately require a final high localized stress to produce catastrophic failure. Furthermore, short segment breaks are not easily detected by consumers (most of which are less than 1 cm) and often fall unnoticed into the sink. But, long segment breaks (along with pulled out hairs) end up in the comb or brush and those are the hairs that bother consumers.

Tress combing experiments when snags produce high combing forces, show that broken hairs can be collected in tens of comb strokes [27, 28] rather than in thousands of comb strokes necessary for fatigue breakage. These combing force facts have been demonstrated in various ways and they clearly demonstrate that high localized stresses created by tangles are the primary cause of hair breakage by impact more so than by fatiguing actions.

10.3.11 Summary of Hair Breakage as a Complex Multifactorial Phenomenon

- Tangle formation is involved with hair fibers looped over other hairs and severe bending deformations as suggested by Brown and Swift [29].
- Hairs are broken by impact [19] generated by pulling a brush or a comb through a tangle producing high localized forces where one or more hairs are looped over another hair or hairs [26, 29].
- The complexity of snags increases with hair fiber curvature [8, 27] producing very high combing forces in both the mid-length and end peak regions.
- The amount of water in the fibers affects combing forces and hair breakage [27]. Straight to wavy hair when combed dry produces higher end peak forces than mid-length forces, but when wet produces higher mid-length combing forces [12] corresponding to where hairs break and to the amount of breakage.
- The work of combing of highly coiled hair is lower wet than dry, but the reverse holds for wavy to straight hair [8, 27] producing more breakage for coiled hair

when it is dry and more breakage for straight to wavy hair when it is wet, corresponding to combing forces.
- Chemical damage by perms, bleaches, permanent dyes [32], straighteners [33] and sunlight exposure [34] weaken hair and increase inter-fiber friction leading to more tangle formation and more breakage. Once again breakage corresponds to combing forces.
- Conditioners reduce combing and brushing forces and have been shown to produce less hair breakage [27] consistent with combing forces.
- Wear by abrasion for straight to wavy hair occurs from combing over the entire fiber, but more near the fiber tips because of a longer residence time, but even more so by high end peak forces when dry [12] as evidenced by an increase in the number of short segment breaks [12, 27].
- Combs or brushes with more space between the teeth or bristles lead to fewer and less complex tangles and therefore to lower combing forces, to less abrasion and fewer broken hairs. Most brushes provide more long segment breaks and fewer short segment breaks than combs [28].

The literature on hair breakage clearly shows that the primary factors involved in hair breakage are the occurrence of tangles created by combing or brushing where at least one or more hair fibers are severely bent around at least one other hair [12, 26, 29]. Furthermore, hair breakage correlates with combing forces. In addition, combing force curves vs. breakage shows that where the break occurs along the fiber corresponds to the higher combing forces in combing force curves. Therefore, highly localized stresses are created by hair on hair impact when one pulls a comb or a brush through a tangle [29]. As a result, one or more hairs break, either with or without flaws, under this condition. Other variables (described above) are clearly involved to determine the actual number of broken hairs and the type of fractures. These variables are described in detail above and include hair type (primarily curvature) [2, 8, 27], hair condition (treatments and wear) and wet vs. dry combing or brushing of the hair and the specific grooming device as explained in the discussion above. Brushing and combing and fatiguing certainly play a role in weakening hair especially for short segment breaks but it is unlikely to lead to a high percentage of fatigue breaks as claimed by Evans and Park [37] unless one broadens the fatigue definition to include anywhere from two cycles to more than millions, but low cycle fatiguing starts at 50,000 cycles and goes down.

10.4 Split Ends, Types, Their Occurrence and Formation

This author carried out a project to identify the different types of split hairs that form on live heads under “normal” usage conditions by consumers. An arrangement was made with a local hair dresser to collect hair clippings from his customers that he judged would likely have split hairs. A questionnaire was completed by the hair dresser in collaboration with the client to provide an idea of the type of hair and the

Table 10.2 Types of split hairs formed on live heads by consumers (in use)

Type of split	Initials of subjects providing hairs for examination								Totals
	DR[a]	LR	LRR[b]	LJR[c]	DC	HD	MB	QC[d]	
Simple small	4	1	8	19	7	5	5	27	76 (27.9%)
Simple large	9	4	8	34	10	9	2	47	123 (45.2%)
Complex	1	0	0	4	9	0	0	10	24 (8.8%)
Split (not at end)	2	1	2	2[e]	4	3	0	20	34 (12.5%)
Split (off step)	1	1[f]	0	4	1	0	0	0	7 (2.6%)
Split (in middle)	1	0	1	4[g]	0	0	0	2	8 (2.9%)
	18	7	19	67	31	17	7	106	272 (99.9%)
Weight hair (g)	2	2	3	10	6	12	1.5	5	
No. splits/g	9	3.5	6.3	6.7	5.2	1.4	4.7	21.2	

[a]Used frosting system on hair periodically for 2 years
[b]Permanent dyed and in sun frequently and for long times
[c]Permanent dyed and once used persulfate system also sunworshipper
[d]Permanent dyed (blonde-white) and sunbleached
[e]One is a complex split
[f]From simple long step of DR hair that broke between photo and micrograph (count step)
[g]One complex split through a knot

different types of treatments and conditions that the hair had been exposed to. Hair cuttings were collected from eight different consumers and the hairs examined initially under a magnifying lens with a light to separate out the split hairs. The splits were then photographed and classified according to the types summarized in Table 10.2.

Figures 10.8, 10.9, 10.10, 10.11, 10.12, 10.13, 10.14, 10.15, 10.16, 10.17, 10.18, 10.19, 10.20 and 10.21 depict the different types of split hairs described in Table 10.2. Figure 10.8 is a magnified photograph of two split ends; the one nearest the lower left corner is a simple small split end while the other is a simple large split end. The legs of the split in each case are nearly equal in length and width; therefore these are called simple split ends. The distinction between the large and the small simple split end is when the length of the legs of the split is about 10 times the width of the hair fiber or longer it is called a large split end. Large split ends can be of three different types: One type is when the two legs of the split are essentially equal in width (Figs. 10.8 and also see 10.9 for an extreme case of a large simple split end). Another type is when the two legs are unequal in width (see Fig. 10.10). A third type is when the two legs are unequal in length and the short leg does not appear to be broken off or when the two legs of the split are unequal and the short leg is broken off (this split is sometimes not distinguishable from a split end off of a step fracture (Fig. 10.11)).

A split end off of a step fracture is illustrated in Fig. 10.11. Kamath and Weigmann [23] described this type of split end in their paper on fractography of human hair. The split end of Fig. 10.12 also appears to be a split end off of a step fracture, although it may have been a simple large split end in which a part of one of the legs broke off. The weakened fibrillated part of the longer leg of the split

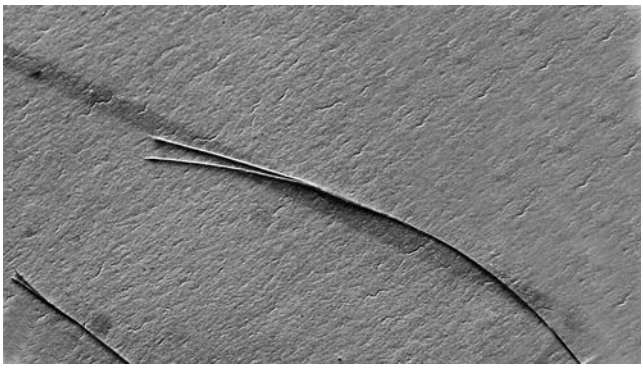

Fig. 10.8 A simple small split end (*lower left*) and a simple large split end

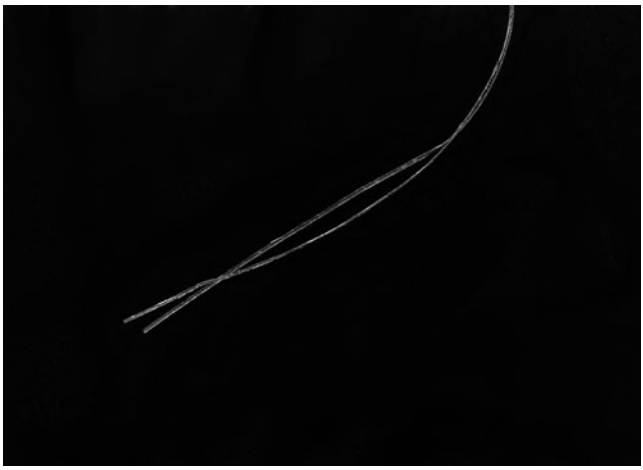

Fig. 10.9 A very large simple large split end

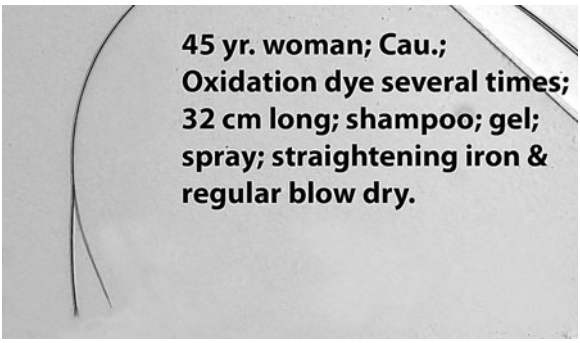

Fig. 10.10 A simple large split end with legs of unequal width

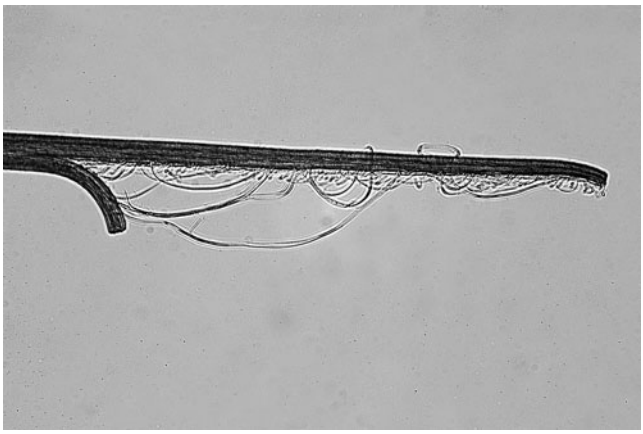

Fig. 10.11 A split end off of a step fracture

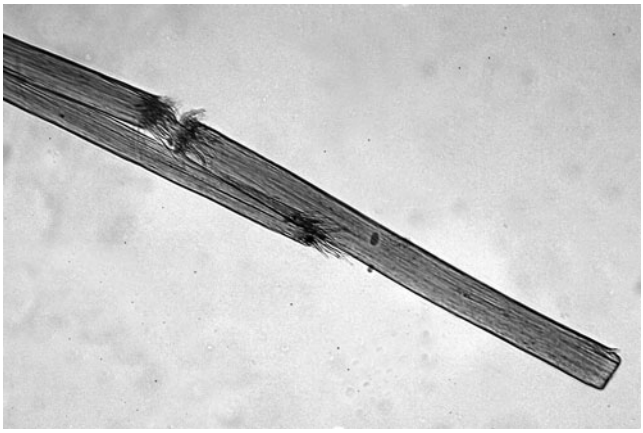

Fig. 10.12 A simple large split end with unequal legs. Note the one leg that is hanging together by fibrils

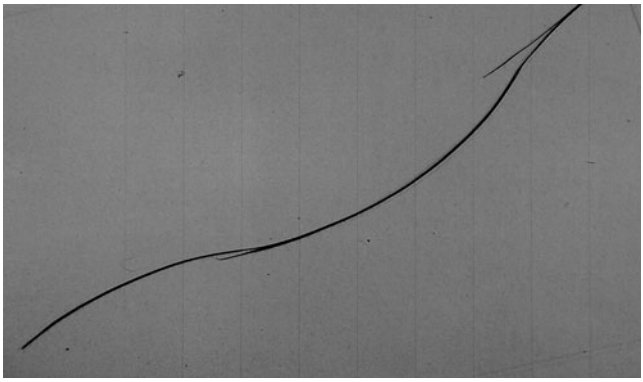

Fig. 10.13 A compound split hair where the splits appear to be independent of each other

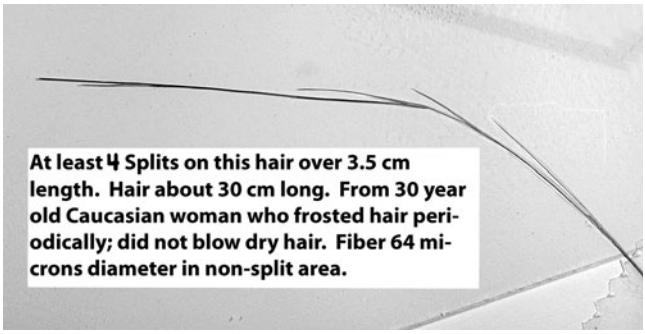

Fig. 10.14 A compound split hair with multiple splits over a 3.5 cm length of the fiber. This hair fiber was taken from the head of a 30 year old Caucasian woman who used peroxide-persulfate bleach on her hair periodically for a period of about 2 years. Her hair was down to her shoulder blades

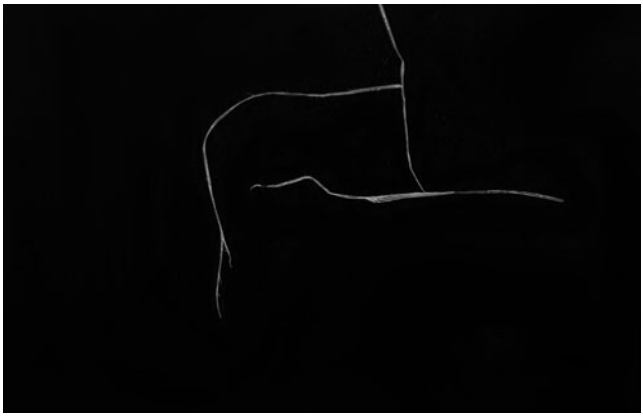

Fig. 10.15 A very large compound split end cut from the head of a Caucasian woman. This woman used permanent dye on her hair periodically and she was a frequent sun bather

appears to be ready to break off. This split resembles the break found in the genetic abnormality Trichorrhexis nodosa described in Chap. 1. It is remarkable that such hairs can still exist on human heads, but all these split ends came from live heads of consumers who used normal consumer or salon hair products on their hair.

Figure 10.13 depicts a complex split end. I define a complex split end as one that has either two or more splits at different parts of the fiber or three or more legs off of a single split end. Figure 10.13 illustrates a hair fiber that contains two different splits that are far enough apart that they appear to be independent of each other. Figure 10.14 is a complex split hair that contains four splits over a 3.5 cm length of hair. Three of these splits appear to be independent of each other. This fiber was found on the head of a 30 year old Caucasian female with shoulder length hair who applied frosting treatment (persulfate-peroxide) to her whole head of hair

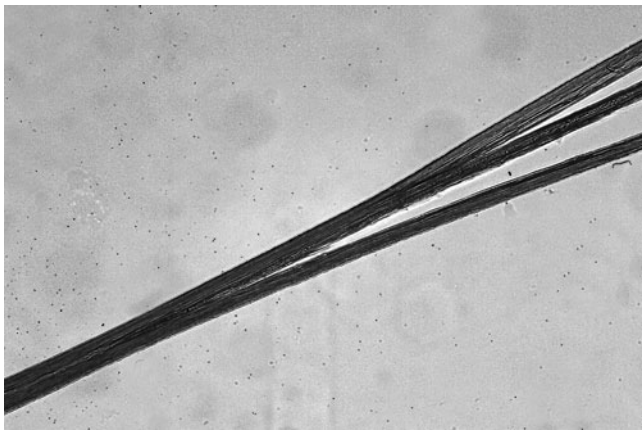

Fig. 10.16 A compound split end with three legs near the origin of the split

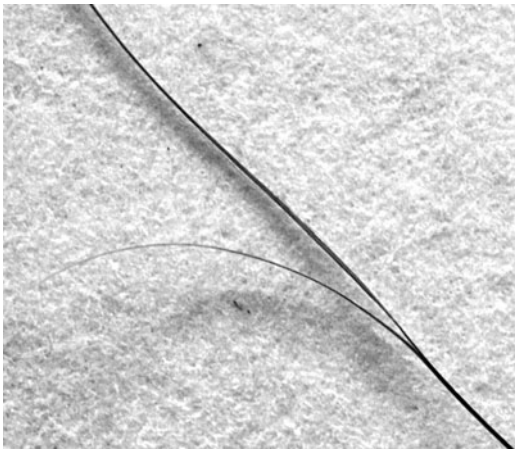

Fig. 10.17 A split hair not a split end. This split was found about 4 cm from the distal end of the fiber

periodically for 2 years. This damaged hair fiber remained on her head and the legs of the splits remained intact without breaking off.

Figure 10.15 is another complex split hair that was found on the head of a Caucasian female with shoulder length hair who had used permanent dye periodically on her hair. This woman was also a frequent sun bather and used a straightening iron on her hair regularly. These three treatments involve free radical reactions. This fiber is another example that I would have expected to have broken off and not be found on the head of a person. Figure 10.16 is another complex split hair in which the three legs of this split originate from or near the split origin.

Figure 10.17 is an example of a split hair that is not at the distal end of the hair fiber. In this case the split occurred about 4 cm from the tip end of the fiber. I have seen cases of this type of split hair in which the distal end of the split is at least 6 cm from the distal end of a hair fiber. In this particular case the origin of the split

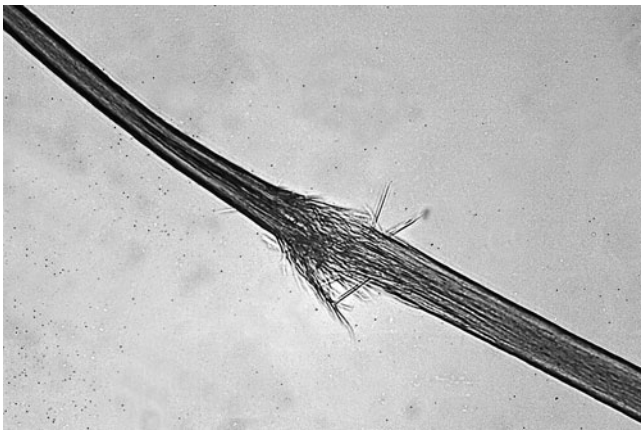

Fig. 10.18 A split hair not a split end where the fiber is held together by fibrils a few centimeters from the distal end

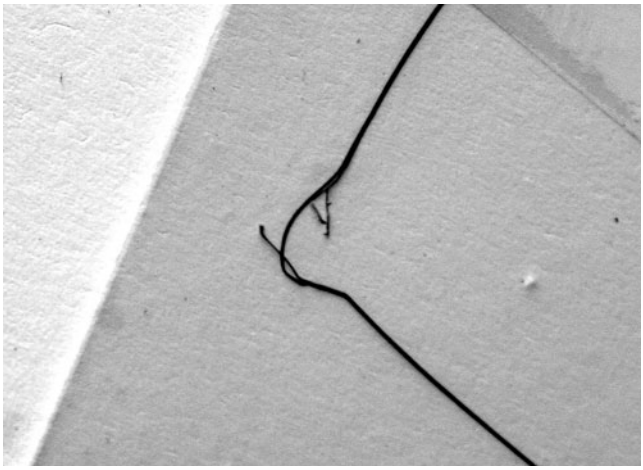

Fig. 10.19 Another split hair not at the end. In this case one end of the split is broken

appears to be close to a twist. This hair was taken from the head of a Caucasian female who treated her hair periodically with oxidation dye. About 1 year prior to cutting, she had a cosmetologist apply a peroxide-persulfate bleach to her hair. She also spent considerable time sun bathing in the Florida sun and regularly used a hot iron straightener and a blow drier on her hair. The oxidation dye, bleach, sunbathing and hot iron all involve free radical reactions.

Figure 10.18 is a split hair (found from the hair of the same woman) in which the fracture site is not at the end. In this case, the fiber has fractured but remains connected by fibrils that resemble the broom-like fractures at the nodes of

Fig. 10.20 Another split hair not at the end where the split is a slit in the hair. This slit-split was found a few centimeters from the tip end of the hair fiber

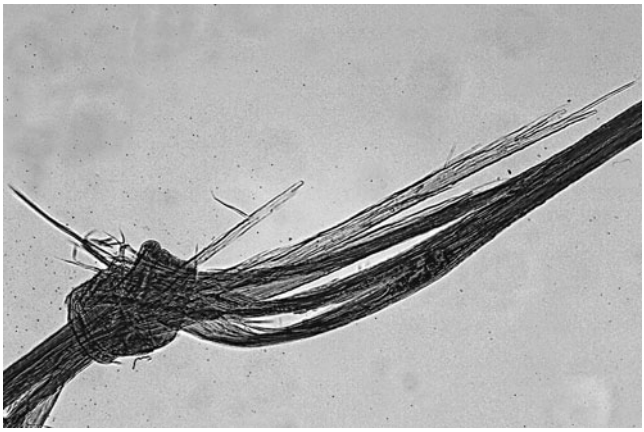

Fig. 10.21 A split fiber at a knot

Trichorrhexis nodosa, see Chap. 3. But in this case the effect is caused by cosmetic treatments and grooming actions, not by a genetic abnormality.

Figure 10.19 is another case of a partially broken hair fiber in which the fracture site is far from the distal end. This woman periodically used permanent dye on her hair and she regularly used a straightening iron on it but indicated she did not sunbathe (two free radical treatments).

The hair fiber depicted in Fig. 10.20 contains a slit far from the distal end. This figure shows the slit at two different magnifications. This split goes completely through the fiber but does not continue to the distal end. This hair fiber was found on a Caucasian woman with shoulder length hair who used permanent dye on her hair,

she sunbathed frequently and regularly used a straightening iron on her hair; once again three free radical treatments.

Figure 10.21 is an example of a split hair at a knot. Several knots were found in the hair of this Caucasian woman who had curly hair (curl type III by the STAM procedure). This woman regularly used a straightening iron on her hair and periodically used permanent hair dye and a peroxide-persulfate bleach system had been applied to her hair by a hair dresser. She also occasionally sunbathed. In each case where I examined knots under the light microscope I could see varying amounts of fibrillation at or near the site of the knot. Figure 10.21 depicts the most extensive fibrillation that I observed at a knot.

10.4.1 Hair Treated with Free Radical Cosmetics and Sunlight are Susceptible to Splitting

The data of Table 10.2 shows that the highest incidence of splits (splits per gram of hair) and the most severe splits occurred on the hair that had received both a bleaching treatment (oxidation dyed or bleached) and frequent sunlight exposure. The one exception is the hair that was treated with a peroxide-persulfate frosting treatment (another free radical system) multiple times over a 2 year period. All hair samples were shoulder length or longer. So, a common factor in the hair with the most severe and most splits involved extensive free radical attack on the hair.

Robbins [38] described the cortex-cortex cell membrane complex as the area of the fiber that is most sensitive to free radical attack, because of its multiplicity of double bonds (allylic groups) and tertiary hydrogen atoms. This conclusion is consistent with the conclusion of Kamath and Weigmann [23] in their paper on fracturing of human hair and with the paper by Swift [39] on split end formation. Kamath and Weigmann [23] observed that the cortex-cortex cell membrane complex serves as an area for the axial propagation of cracks which can ultimately lead to split hairs.

Zimmerman and Hocker [40] in their studies on radiation of wool fibers showed that wool fibers that were not irradiated, when fractured, provided mainly smooth or cut fractures. Wool fibers that received short and intermediate term exposures to simulated sunlight when fractured provided mainly step and split fractures. However, after long times of irradiation (approaching unrealistic exposures for hair on heads) when fractured the fibers provided amorphous fractures. Therefore, the cortex-cortex cell membrane complex after it has been damaged by exposure to free radical reactions is prone to crack formation and the splitting of hairs.

The types of free radical reactions that commonly occur on live heads are in sun exposure, bleaching with either peroxide-persulfate or peroxide where copper or iron is present (including permanent dyeing) and/or hair that has undergone a large number of exposures to heat treatments such as hot curling or straightening irons. These effects have been confirmed by the types of hair most prone to split end formation on live heads described in Table 10.2.

10.4.2 Causes of Split Hairs and Split Ends

Among the more important scientific papers with regard to splitting of hairs are the hair fracturing studies by Kamath and Weigmann [23, 24], the paper describing a mechanism for split end formation by Swift [39], the hair breakage study by Brown and Swift [29], the study of irradiation of wool fiber by Zimmerman and Hocker [40] and the hair breakage studies by Robbins [19, 26] and by Robbins and Kamath [27, 28].

The literature provides the following conclusions with regard to split end formation:

1. Split hairs form more readily in the dry state than the wet state, particularly from 30% to 65% RH [23]. In addition, this author has shown in unpublished work that split ends are formed more readily from dry combing than from wet combing.
2. Splits form more readily on oxidized hair (see Table 10.3) and on damaged hair in general [29, 39, 40]; also see Table 10.3. The use of conditioners decrease split end formation, see Table 10.3. The evaluation of split hairs taken from heads shows that fibers that have been exposed to photochemical and chemical bleaching and in some cases also treated with straightening irons (free radical type exposures) are susceptible to split end formation.
3. Paragraph 2 supports this conclusion that the cortex-cortex cell membrane complex serves as a route for the propagation of axial splits in the fiber and for the formation of split ends [23, 38].
4. Splits form more readily on abraded [19, 23] and or weathered hair [29, 39], that is, hairs in which large sections of cuticle have been removed [23].
5. There is a stronger association between short segment breaks and split ends than long segment breaks and split ends (see Table 10.4).

Table 10.3 Effect of chemical bleaching and conditioning on split end formation and on long and short segment breaks after combing at 50% RH

Hair type and treatment	Split ends[a]	Short breaks[a]	Long breaks[a]
Bleached + shampoo + conditioner	2	112.7	18.7
Unaltered control + shampoo	16.3	186.7	27
Bleached + shampoo	24.3	328	102

[a]Means of three tresses; all three means in each column are significantly different from each other

Table 10.4 Cross-cutting vs. taper cutting and split end formation (60% RH)

Type cut	Split ends[a]	Plus splits[b]	End peak force[c]	Short segment breaks[a]
Cross-cut	47.5	3.5	130	799
Taper cut	18	1.5	23	253

[a]This is the number of split hairs that are not split ends at 100 comb strokes
[b]In grams load for 17.8 cm comb stroke and 3 g tresses for Caucasian hair
[c]This end peak force of cross cut hair is about five times that of taper cut hair

6. Split hairs form more from bending [29, 39] or impact loading [19] than from extension actions [29, 39].
7. Cross-cutting hair tresses or a switch so that all of the fibers are essentially of the same length increases the number and severity of splits, see Table 10.4.

The data of Table 10.4 shows that cross cutting the hair so that the ends of the hair are nearly equal in length vs. taper cutting the hair (ends are of different lengths) increases the number of split ends nearly threefold. As expected, the end peak force in quantitative combing also increases by cross cutting the hair. In this case the increase was by a factor of about 4. In another study the end peak force was found to correlate with short segment breaks and the data of Table 10.4 shows a directional effect between split ends and short segment breaks. The split end data of Table 10.3 was obtained on hair tresses that had been used in a breakage study where short and long segment breaks were also counted. These data were analyzed by analysis of variance providing a significant relationship between short segment breaks and the number of split ends; however, the relationship between long segment breaks and split ends was not significant. This analysis suggests a relationship or a connection between short segment breakage and split end formation. In addition, previous data on similar types of hair and similar tresses shows that the end peak force increases by a factor of about 5 (Table 10.4) by cross-cutting hair vs. taper cutting.

These results (Table 10.4) suggest that the end wrapping mechanism described by Robbins and Kamath [27] for formation of short segment breaks is likely involved in the formation of split ends. Before combing, hairs exist in complex interwoven patterns and the curlier and longer the hairs the more complex the interweaving. As the comb descends through the hair, sections of hair above the comb are made parallel. Those hair fibers beneath the comb are either made parallel or entangled. Entanglements occur by hairs looping around other hairs, or hairs looping around comb teeth and other hairs between the comb and the distal tips of the fibers.

As the comb continues to advance through the looped/entangled hairs long segment breaks occur. As the comb approaches the tips (when the hair is dry) wrapped ends result. End wrapping of hairs around comb teeth and other hairs occurs by inertia and possibly static charge. End wrapping produces a high end peak force resulting in high abrasion and severe bending deformations along with impacting and fatiguing all resulting in short segment breaks ($<$2.5 cm). Short segment breaks are more numerous if the hair is cross cut compared with a tapered cut or if the hair is damaged wherein inter-fiber and hair on comb friction is higher.

Split ends form from a crack in the cortex-cortex cell membrane complex as a result of severe bending deformations [39] and hair on hair impacting [19, 28] in wrapped ends. The crack propagates to the end of the hair particularly on highly abraded hair wherein some cuticle has been worn away. Two schemes [23, 39] described in the literature for split end formation are described below.

10.4.3 Mechanisms for Formation of Splits

The formation of split hairs has been either directly or indirectly studied by several different scientists. Since so many different types of split hairs have been identified (Figs. 10.8, 10.9, 10.10, 10.11, 10.12, 10.13, 10.14, 10.15, 10.16, 10.17, 10.18, 10.19, 10.20, 10.21), more than one mechanism is likely to be involved to account for the different types of splits.

The literature suggests that split hairs can form from bending [39] and from stretching actions [23] although Swift suggests that bending actions are more important than stretching on heads. From an examination of the hair literature and the seven factors above that promote or lead to increased split formation, I conclude that split hairs form more readily from abrasion in combination with impact loading involving bending and or torsional deformations.

Swift [39] provided the following mechanism for the formation of split hairs. He explained that snags form as the comb approaches the distal ends of the hair. When this occurs hairs become increasingly bent over each other and comb teeth (end wrapping occurs). Swift explained that since most hairs are elliptical they will bend about the plane of the major elliptic diameter. Upon bending, shear stresses will be parabolic and distributed across the minor axial diameter with a maximum at the plane containing the major axial diameter. Shear fracture then occurs which tends to propagate toward the tip end by the continued bending and straightening of the hair. This author believes that Swifts mechanism does occur with highly elliptical hairs that are damaged, but other mechanisms are operable under other conditions.

Kamath and Weigmann [23] also offered a mechanism for split end formation in their paper on hair fracturing. This mechanism does not favor or preclude any fiber shape from the formation of split ends. Kamath calls this mechanism "shock-wave" splitting. I discussed this mechanism with Kamath while we were working together on hair breakage. According to the mechanism of Kamath, "shock-wave" splitting occurs at low humidity when the fiber is impacted and deformed in a snag and when the cuticle is damaged and weakened.

The following mechanism is what I have taken from these discussions and I have merged Swift's and Kamath's mechanisms in the following manner. When the comb approaches the distal ends of the hair, end wrapping occurs and relatively high forces are applied to move the hair through the ends. This likely involves bending actions and as Swift proposed since most hair fibers are elliptical bending will occur about the plane of the major axial diameter. At that instant primarily through impact loading and severe bending deformations a crack is formed in the cortex. Residual elastic energy then dissipates like a shock wave in a radial plane at the fracture faces. The shock wave is then propagated axially through the damaged cortex-cortex cell membrane complex forming the split hair or split end. Furthermore, splitting is most prone to occur at low RH and when the fiber is damaged (both in the cuticle and in the cortex-cortex cell membrane complex). When the cuticle is damaged and weakened that is highly abraded with badly worn tip ends so that there are too few cuticle layers to strongly hold the ends together and the cortex

cell membrane complex has been highly oxidized by free radical chemistry the "shock wave" propagates rapidly to the end of the fiber. Thus, this phenomenon is associated with short segment hair breakage explaining the correlation of short segment breaks with split ends.

10.5 Flyaway Hair

10.5.1 Static Charge and Flyaway

When a comb is brought into contact with hair at low RH, charges of opposite sign but equal magnitude are generated on both the comb and the hair surface. The charges are generated because of the difference in the affinity of each of these materials for electrons (electrochemical potential). The repulsive forces of static electricity on the hair cause the fibers to separate producing Flyaway Hair [1]. Static electricity consists of electrons or ions that are not moving. It results from rubbing and pressure during combing and brushing between two poorly conducting surfaces. An electric charge from friction is called triboelectricity; that from pressure is called piezoelectricity.

After combing or after separation of the comb from the hair, the dissipation of the static charge is governed by the conductivity (reciprocal of resistivity) of the fibers or their electrical resistance. In general, materials with a high electrical resistance such as human hair, wool, silk, or nylon are more prone to static buildup than are lower-resistance materials like cotton and rayon [41]. Therefore, the phenomenon of static flyaway is concerned with three conditions:

- Static charge generation on the fibers,
- Conductivity or the removal of static charge from the hair, and
- Hair type.

The primary factors involved in static charge generation are (1) the difference in electrochemical potentials of the two surfaces, and (2) the rubbing forces involved. For example, the use of lubricants can reduce rubbing forces and in that manner provide less charge generation [6]. Jachowicz et al. [14] determined that the conductivity of the hair surface is also important to static flyaway. These scientists demonstrated that long-chain quaternary ammonium salts increase the conductivity of the hair surface in addition to decreasing hair fiber friction. For these two reasons, long-chain quaternary ammonium compounds are excellent antistatic agents.

Hair type is also relevant to the condition of flyaway hair. For example, hair fiber curvature is critical to flyaway. Robbins [6, 42] proposed that by the C^2 hypothesis, at high curvature (for example, Curl types IV–VIII), flyaway hair would be minimal or nonexistent. This lack of flyaway is because the entanglements created by high curvature hair will dominate over the ability of the fibers to separate from static

charge. He demonstrated that tresses of Caucasian hair steam set to Curl type V had no flyaway in spite of a high static charge build-up. On the other hand, hair tresses of Curl type II with the same static charge generated extreme flyaway. Furthermore, when the two hair tresses were brought together, the flyaway fibers of Curl type II were repelled by the entangled hairs of the Curl type V tress. This effect proves that the higher curvature hair did have static charge build-up capable of producing flyaway, but not on highly coiled hair. This experiment also supports the hypothesis [6, 42] that at high degrees of curvature, curvature dominates the hair assembly property of flyaway hair as it does for so many consumer hair assembly properties.

10.5.2 Methods Relevant to Static Flyaway

Mills et al. [43] described two techniques for estimating static charge on human hair. The "ballooning method" actually estimates static flyaway. This method consists of acclimating tresses at a desired low humidity in a chamber (generally for 24 h) and then combing the hair in a controlled manner. The relative amount of static charge is then estimated by the amount of ballooning or separation of the fibers of the tress (see Fig. 10.22). The second method of Mills et al. [43] consists of first acclimating tresses, then combing them in a controlled manner with a special comb containing a bare copper wire in its back. The copper wire leads through an insulated holder to an oscillograph. The charge on the comb is measured, and theoretically it is equal and opposite to that on the hair.

Barber and Posner [44], Lunn and Evans [13], and Jachowicz et al. [14] have all described similar yet more sophisticated approaches. Lunn and Evans [13] described methods for measuring charge generation on hair tresses, charge mobility on the hair, and charge distribution along the hair fibers. These methods involve

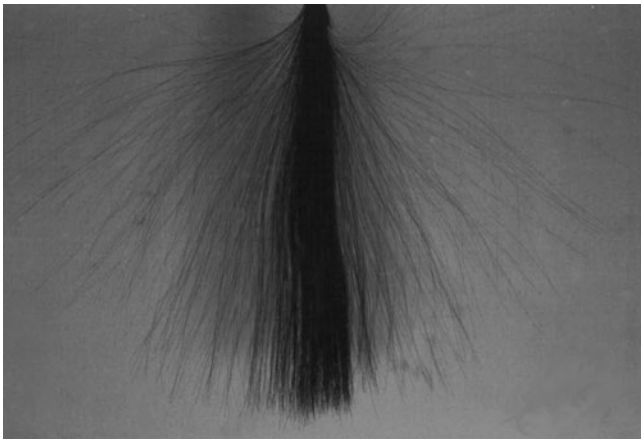

Fig. 10.22 Static ballooning of hairs in a tress due to static charge build-up

combing hair tresses to induce the charge. Jachowicz et al. [14] developed a useful method to measure both charge generation and charge decay by rubbing hair fibers against different elements under controlled conditions. Jachowicz et al. also measured charge density along the length of tresses and showed that the electrical field that concentrates near the fiber tips causes flyaway hair.

The measurement of static charge on textile fibers, fabrics, and yarns has also received a considerable amount of scientific attention and is relevant to this same subject on human hair. The book by Meredith and Hearle [45] provides a good introduction into this subject. Electrical resistance (reciprocal of conductance) of fibers is also fundamental to their static electrification and is described by Hersh [46] for human hair and other fibers and by Meredith and Hearle [45] for textile fibers.

10.5.3 Triboelectric Series

Attempts have been made [47, 48] to classify materials according to "triboelectric series" which lists materials in an order so that the higher one on the list will be positively charged and the lower one negatively charged when any two of the materials are rubbed together. In theory, triboelectric classifications should be useful, because the relative affinity for electrons of each of the materials in contact (electrochemical potential) is very important to the charge developed [13]. However, such series are generally not very consistent.

10.5.4 Moisture Content and Resistance

The moisture content of human hair provides a large influence on static charge. Increasing moisture in hair decreases its electrical resistance [46]. Therefore, increasing moisture increases the conductivity of the fiber surface so that it is less prone to develop a static charge because the electrons distribute more evenly over the entire hair surface.

The electrical resistances of wool and human hair have been shown to be very similar at 85% RH (see Table 10.5), and their resistances are similar from 52% to 85% RH [49]. Since the moisture binding-RH relationships of wool and human hair from 0% to 100% RH are virtually identical (see Table 9.33), their resistance-RH relationships from 0% to 100% RH must also be very similar. Morton and Hearle

Table 10.5 Electrical resistance of wool and human hair at 85% RH [46]

Wool	$4.2–7.4 \times 10^{12}\ \Omega$
Human hair	$10.0–17.0 \times 10^{12}\ \Omega$

Table 10.6 Effect of RH on the static charge developed on human hair for a shampoo and a crème rinse conditioner[a] [43]

	% Relative humidity		
Treatment	27% RH	51% RH	76.5% RH
Experimental shampoo	14.3[a]	10.8[a]	3.3[a]
Creme rinse	2.5[a]	1.5[a]	0.4[a]

[a]Data are relative pip heights from oscillograph recordings of the charge developed on the comb

[41] described the resistance of wool fiber to vary by a factor of approximately 10^5 from 10% to 90% RH and by a much larger factor from 0% to 100% RH.

Confirming this relationship of resistance-RH and static charge for human hair is the effect of RH on static charge shown by Mills et al. [43] (see Table 10.6). These data show a progressive decrease in the static charge developed on the hair with increasing RH, for each of two different types of treatment. For both treatments, the principal effect of RH is to increase the water content of the hair. Increasing the water in the hair surface decreases its electrical resistance, making the fiber a better conducting system and therefore less capable of retaining a static charge.

10.5.5 Temperature and Static Charge

The resistance of keratin fibers generally decreases as temperature increases. An increase of 10°C will produce approximately a fivefold decrease in resistance [43]. Therefore, the perceived effect of temperature on conductivity does not appear to be the cause of greater flyaway from hot combing as compared to room temperature combing.

10.5.6 Impurities on the Fiber Surface can Influence Static Charge

For hygroscopic fibers like wool fiber and human hair, the resistance can be influenced by electrolyte content. For example, the addition of potassium chloride lowers the resistance of wool, whereas washing in distilled water can increase wool's resistance [43] by removal of electrolyte from the hair surface layers.

10.5.7 The Amount of Static Generated is Virtually Independent of Rubbing Velocity

Hersh's [46, 48] studies with textile fibers suggest that the amount of static charge generation is virtually independent of rubbing speed, when rubbing one high-

resistance fiber against another high-resistance fiber. However, Cunningham and Montgomery [50] have shown an increase in static charge with increasing rubbing velocity when rubbing high-resistance fibers against metal fibers. Rubbing velocities in both these studies were approximately 1–30 cm/s.

10.5.8 Decreasing Rubbing or Combing Forces Decreases Static Charge

After tresses are shampooed and combed, the amount of static ballooning also depends on the amount of combing. As already indicated, Lunn and Evans [13] concluded that the primary way that long-chain quaternary ammonium salts reduce static buildup is by decreasing inter-fiber friction which in turn reduces the work of combing. Therefore, one way to reduce static buildup is to reduce the work of combing, which is to make the hair comb easier [44].

10.5.9 The Sign of the Charge is Related to the Direction of Rubbing

The sign of the static charge that develops on both human hair and wool when rubbed against similar fibers has been shown to be related to the direction of rubbing [14, 46, 51]. If the fibers are oriented in the same direction and one fiber is removed from the bundle by pulling it out by its root end, a positive charge develops on this fiber. If a fiber is removed from the bundle by pulling it by its tip end, a negative charge develops on the fiber. If the fiber that is removed is oriented opposite to the other fibers of the bundle, or if it contains no scales, no charge develops on it. Although this effect is not fully understood, it has been attributed to the heterogeneity of the scales. The points of the scale edges have been suggested to have a different triboelectric nature from the main scale surfaces. Therefore, rubbing a fiber root to tip rubs primarily against scale surfaces, whereas rubbing tip to root rubs mainly against scale edges [46].

An equally interesting effect on the sign of the static charge on hair has also been found to relate to the nature of surface deposits or treatments [14, 41]. Washing hair tresses with an anionic shampoo and drying at low relative humidity and then combing produces a large amount of static ballooning. Flyaway was considerably less for tresses treated with a cationic creme rinse followed by water rinsing and drying. However, if tresses were treated with a cationic creme rinse and not rinsed or only lightly rinsed with water, a relatively large amount of ballooning was apparent. Furthermore, the charged fibers from this treatment were attracted to (not repelled from) charged fibers from the anionic shampoo treatment, indicating

opposite signs of static electricity. This different sign for the charge was confirmed by oscillographic measurements. Jachowicz et al. [14] described related effects.

For discussion and theoretical explanations and controversies on the static electrification of fibers, see the book by Morton and Hearle [41], the thesis by Hersh [46], and the paper by Jachowicz et al. [14].

10.5.10 Effect of Ingredients on the Static Charge

Table 10.6 describes the effects of shampoos (high cleaning) compared with creme rinses on the development of static charge on hair. The amount of charge developed by combing or brushing hair tresses (straight to wavy hair) is related to the amount of flyaway. The amount of flyaway generated is related to both the chargeability (charge generation and conductivity combined) of the hair fibers and to the work of combing. The lower static values (see Table 10.6) for both creme rinse and shampoo treatments as a function of RH are due primarily to a decrease in the electrical resistance of the hair, and the lower work of combing, as well as the increased moisture content (see Table 9.32). When the resistance drops below a certain value near 10^8 Ω-g/cm^2, the charge can apparently spread more readily over the entire hair to adjacent surfaces and dissipate into the air. In this manner, the charge density required to cause noticeable flyaway is not exceeded.

Jachowicz et al. [14] found that the adsorption of long chain quaternary ammonium compounds, cationic polymers, and some specific polymer-detergent complexes decreased the electrochemical potential and increased the conductivity of hair. Of course, long-chain quaternary ammonium compounds also decrease the rubbing forces by a lubricating action. This lubrication decreased the charge generated, and Lunn and Evans [13] suggested that lubrication is the major reason for the antistatic effect of creme rinses. Jachowicz et al. [14] suggested that the increase in surface conductivity by quats in creme rinses is also important to the effectiveness of these ingredients as antistats. Therefore, the lower static charge for creme rinse vs. shampoo treatments (Table 10.6) is a result of lower frictional drag during combing as well as an increase in the conductivity of the hair. The change in resistance (of keratin fibers) from 10^{12} to 10^8 Ω-g/cm^2 that occurs between 22% and 77% RH (Table 10.7) approximates the required decrease in resistance for a creme rinse effect at 27–76% RH (Table 10.8), assuming that a large part of the antistatic effect by creme rinses is due to an increase in conductivity.

Table 10.7 Effect of relative humidity on electrical resistance of hair

% RH	Approximate R_s for wool[a] [46]
27	10^{12}
77	10^8

[a]R_s = resistance in ohms between the ends of a specimen 1 cm long and of mass 1 g (ohm-g/cm^2)

Table 10.8 Effect of creme rinse and RH on static charge in hair [43]

	27% RH	76% RH
Shampoo	11.5–14.3	2.2–3.3
Rinses	2.0–3.8	0.4–0.5

[a]Data are relative pip heights from oscillographic recordings of charge on the comb

Jachowicz et al. [14] modified hair fibers by reduction, bleaching, and oxidation dyes and found only a small difference in triboelectric charge vs. chemically unaltered hair and no increase in surface conductivity by these treatments.

10.6 Hair Shine or Luster

Consumer research suggests that hair shine is a more meaningful cosmetic term to consumers than luster. The word luster is used more frequently in scientific works on textile materials. In most of our work on this important cosmetic property, the objective was to develop methods to correlate with the consumers' subjective assessment of hair shine. The words shine and luster are used interchangeably in this discussion.

When hair is illuminated, the incident light may be reflected at the surface or refracted (bent) (see Fig. 10.23). It may enter the fiber and be absorbed (by pigment), or it may reemerge, usually after hitting the rear wall of the fiber, where it is partly reflected and refracted again. The phenomenon of light scattering is a major subject of this section, and we shall see how reflection of light may either enhance or reduce hair shine, how refraction of light can reduce hair shine, and how absorption of light can enhance it.

10.6.1 The Scale Angle and the Specular to Diffuse Reflectance Ratio

Light striking hair in a root-to-tip direction at an incident angle of 30°, provides a specular reflection of 24° (large peak of Fig. 10.24), rather than 30°. The specular reflectance may be estimated from light-scattering curves (Fig. 10.24), primarily from the specular peak height. If the axis of the hair is 30° relative to the incident light, then the scale angle must be 3° (30–2 × scale angle = 24°). The second peak (lower peak) of Fig. 10.24 occurs at approximately 40°, and represents light that has entered the fiber and is reflected from the back wall of the hair. This second peak is much larger for blond hair (dashed line) than for dark brown hair (solid line) because of the greater absorption of light in the cortex by the additional pigment granules of the darker hair.

When incident light strikes a surface, it may be reflected specularly (S), when the angle of reflectance equals the incident angle (which increases shine), or it may be

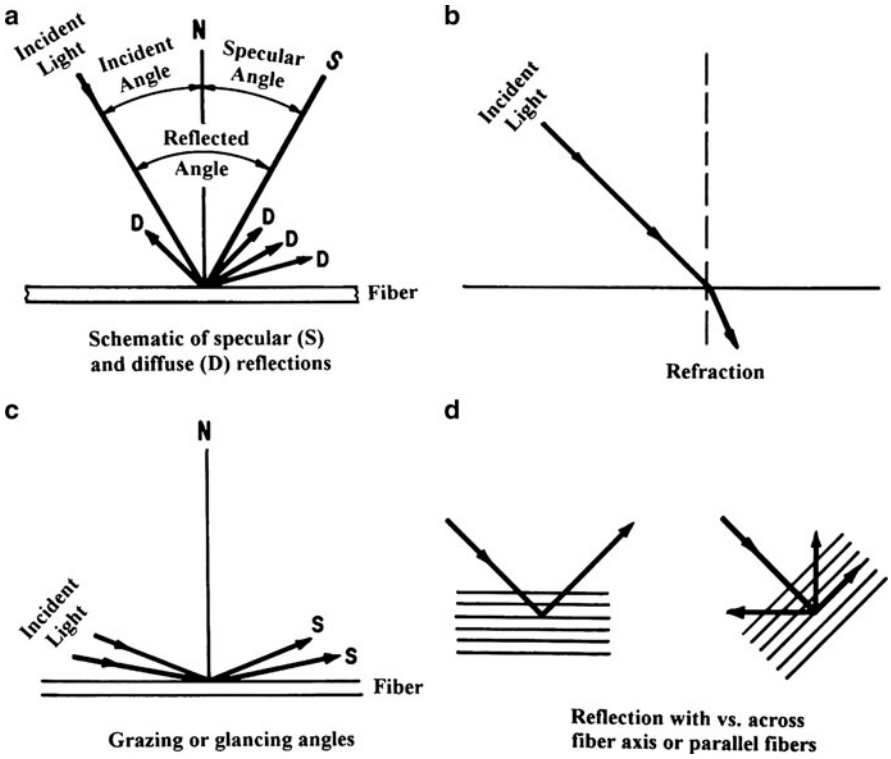

Fig. 10.23 Some parameters important to hair luster

reflected diffusely (D), at angles other than the incident angle (scattered light decreases shine) (see Fig. 10.24). Unless one examines a perfect mirror, a combination of both specular and diffuse reflection takes place.

Diffuse scattering may be estimated from light-scattering curves by drawing a line between the light intensities (voltages of Fig. 10.24) at 0–75° and measuring the area under the line. A light scattering curve with an incident light of 30° striking the fiber in a tip to root direction, shows the back wall reflection near 15° and the specular reflection at 36°, once again suggesting a 3° scale angle.

Some ratio of specular to diffuse reflectance is generally accepted as a measure of luster for fibers and yarns [52–54]. Ward and Benerito [52] determined that the ratio of specular to diffuse reflectance for cotton fibers correlates with visual luster assessments. Fourt [53] suggested a contrast ratio for evaluating luster of wool fabric, using a ratio of specular reflectance at a 45° angle of incidence to diffuse reflectance at 0°. Stamm et al. [55] suggested the function:

$$\text{Hair shine} = (S - D)/S$$

where S = specular reflectance and D = diffuse reflectance.

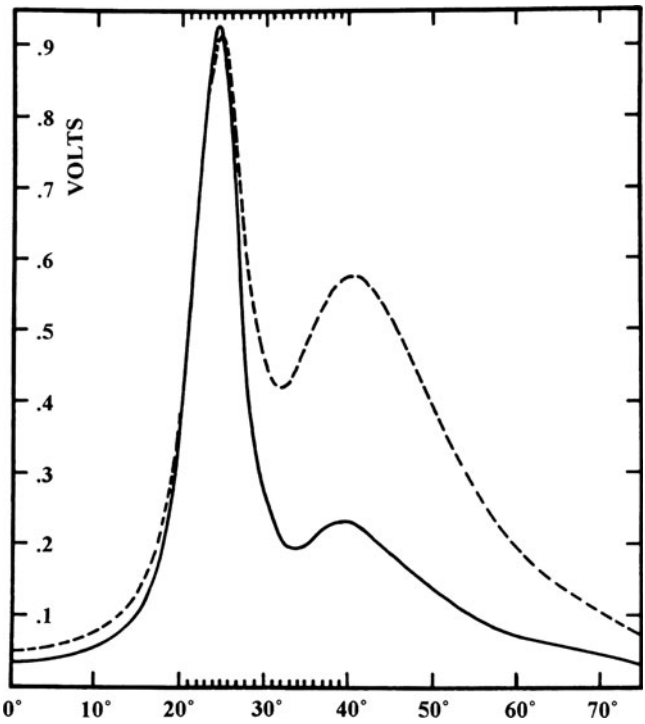

Fig. 10.24 Light-scattering curves from dark brown hair (*solid line*) and blonde hair (*dashed line*) [58] (Reprinted with permission of the Journal of the Society of Cosmetic Chemists)

10.6.2 Hair Shine Methods

Hair shine may be evaluated subjectively on tresses or on heads of hair (preferably on half heads), or it may be evaluated instrumentally. The subjective evaluation of hair shine on tresses can be very consistent and reliable, provided care is taken to consistently align the fibers of the tresses, to control lighting, to use multiple observers to evaluate tresses, and to use replication. Figure 10.25 is a photograph of a board constructed to help align the fibers of a tress consistently and to orient the tresses with respect to the lighting. This board also helps to keep the tresses aligned during the evaluation period. Six tresses seem optimal for any single test. Therefore, only two to three treatments can be evaluated at a time. The data should be analyzed by a nonparametric procedure such as the Friedman or Kruskal Wallis test [56].

Similar care should be taken for subjective analysis of shine on live heads. The primary variables to control for evaluating shine on live heads are lighting and hair alignment [57]. Alignment can be controlled to a limited degree by parting the hair in the center of the head and blow-drying the hair while combing it straight after

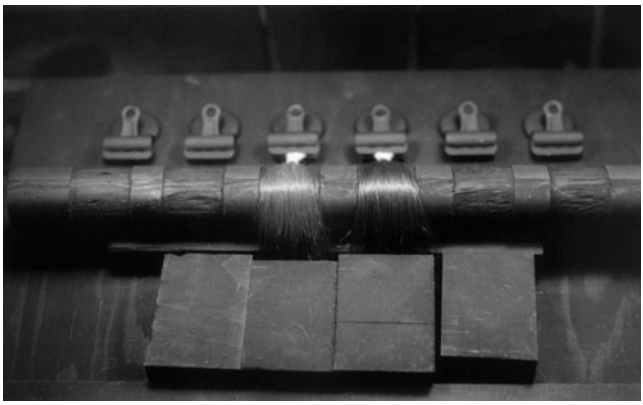

Fig. 10.25 Tress holder developed for panelists assessment of hair shine

treatment. A useful system is to treat hair on heads and to take 30–40 fibers per side after treatment and to evaluate the fibers instrumentally for shine by light scattering.

Several different instrumental methods and approaches have been used to evaluate the shine of human hair [45, 54–62] (Schebece and Scott, private communication). The method of Thompson and Mills [54] measures reflectance from an assembly of hair fibers; the methods of Stamm et al. [55] and Reich and Robbins [58] measure light scattered from either single hairs or from a parallel array of taut hair fibers. The method of Schebece and Scott (private communication) measures light reflected from single hair fibers alone. The method of McMullen and Jachowicz [60] takes digital images of tresses and analyzes the data with special software.

The method of Thompson and Mills [54] illuminates a small tress of hair after the fibers have been carefully aligned over a cylinder 4 in. in diameter. A photocell is placed at an angle of 160° to the incident beam, and at varying distances from the hair sample. The hair is rotated to give a maximum reading. The light source is at a fixed distance (10 in.) from the hair sample. From these parameters, both the specular (S) and diffuse (D) reflectance can be calculated using the following expression, after taking readings at more than one sample to photocell distance (X). In this case, Cos C is the cosine of 80°.

$$\text{Intensity of light reflected} = \text{S}\frac{\text{D cos C}}{\text{X}^2}$$

The limitations of fiber alignment—the inability to vary incident angle or to scan all reflected light from the surface—with the Thompson and Mills method are solved by the goniophotometric methods of Stamm et al. [55], Schebece and Scott (private communication), and Reich and Robbins [58]. From a strip chart recording of intensity of reflected light vs. angle of observation (see Fig. 10.24), the specular reflectance and diffuse reflectance are obtained. Currently the best function for hair shine is this one by Reich and Robbins [58]:

$$L = S/DW(1/2)$$

where S is the specular reflection, D is the diffuse reflection and W(1/2) is the width of the specular peak at half-height.

Most quantitative methods to measure hair luster have relied on goniophotometric measurements of either single hairs or an array of parallel hairs using some function of the ratio of specular to diffuse reflection [55, 58]. Although tresses have been employed for measurement of luster [54] no one had successfully adapted this method to measure luster on curly African type hair tresses. However, McMullen and Jachowicz [60] described a novel luster method that shows promise for measuring luster on curly African hair as well as on curly Caucasian and Asian hair. In this method, the authors recorded digital images of hair tresses with a digital camera coupled to a macro lens. They then analyzed the photographs using special software (Image Tool 2.0 from the University of Texas Health Science School) that took into account the number of reflection sites and their shapes. This method was capable of showing that sebum dulls African hair and it appears to show promise as a means for measuring luster on many types of hair even curly hair. Even though I have a concern about potentially large variances in measuring luster in curly hair or whole heads of hair (because of variable hair alignment), this approach appears to offer promise for a solution to this difficult problem.

10.6.3 Fiber Alignment, Orientation, and Hair Shine

When hair fibers of an assembly are aligned parallel, maximum specular (mirror) reflectance can be obtained with minimum scattering [54]. The problem of consistently aligning the fibers of a tress or hair on the head the same repeatedly or sufficiently parallel perhaps produces the largest variance in shine evaluations. As a result, alignment interferes with the ability to see small changes in hair shine, thus, the obvious advantage of the instrumental methods that evaluate either single hairs or a parallel array of hairs [55–59].

Keis et al. [59] described the effects of hair fiber curvature on hair luster and on hair of different populations. They explained that high curvature hair in an assembly generally displays low luster because it interferes with a uniform parallel alignment of fibers and thereby increases the amount of scattered light. This light scattering effect suggests that luster will generally decrease with increasing fiber curvature unless the curls are broad and synchronized in alignment as often occurs in Curl types II and III.

10.6.4 Shine Increases with Ellipticity but Decreases with Curvature and Twists

Keis et al. [59] worked with African American hair with an ellipticity index of 1.6 frequently found in curl class IV. Keis, Ram and Kamath also concluded that in

addition to curvature, twists and kinks decreased luster because twists increase light scattering. Keis et al. [59] found that by comparing single hair fibers that were straightened in the goniophotometer (to eliminate curvature) that luster increased with fiber ellipticity and with increasing pigmentation. They further demonstrated with an 80 μm nylon fiber with an ellipticity index of 1.0 that when it was mechanically flattened to increase the ellipticity from 1.0 to 1.35 to 7.0 that luster increased because the amount of scattered light decreased. This luster effect occurs because specular light is reflected from the surface of the fiber and light that enters the fiber is scattered by reflecting off of irregularities on the fiber interior.

Apparently this effect of ellipticity on improving luster is smaller at higher curvatures than the misalignment effect at higher curvatures, because assemblies of such hair fibers (Curl type IV–VIII) are generally less shiny than well aligned wavy or straight assemblies of hairs (Curl types I–III) of lower ellipticity. Therefore, Keis et al. [59] agreed with Robbins C^2 hypothesis [6, 42] that when curvature is high, it dominates luster as it does with other physical properties in its influence on hair assembly behavior.

In a single hair method or in an assembly, shine is always more apparent along the fiber axis than across it (Fig. 10.23). When the incident light is in the scale direction, reflectance is at a maximum, and scattering is less than it is in the "against scale" direction [55]. The shine of the surface may appear different when illuminated and viewed from grazing angles as opposed to larger angles where highlights are more prominent (see Fig. 10.23).

10.6.5 Dark Hair (Natural or Dyed) is Shinier than Lighter or Gray Hair

Dark hair often appears shinier than lighter hair. This is because part of the light is reflected at the fiber surface, and part enters the fiber and is scattered by reflecting off irregularities of the interior. When that light reemerges, the diffuse component is increased. If the fiber is colored or dyed, some of this diffuse component is absorbed before reemerging, thus reducing it and making the fiber appear shinier [45]. This effect is depicted in Fig. 10.24, comparing light-scattering curves for a dark Brown hair and a blond hair fiber, and has already been described.

Keis et al. [61] studied the effect of natural hair pigmentation on hair luster using a goniophotometer. This study confirmed that increasing hair color reduces light scattering and increases luster. These same scientists examined dyed hair and found a similar but more complicated picture. Dye composition, concentration and penetration depth must be taken into consideration to account for the results. In addition, the luster of hair of different colors is perceived differently by the human eye adding further complications.

There is less pigment in gray hair than in dark hair. Most likely the pigment granules of gray hair are also smaller in size, both actions a result of changes in the

Table 10.9 Effects of shampoos on hair shine (specular/diffuse scattering)[a]

Step 1: Oily hair from scalp containing only sebaceous soil	0.411
Step 2: Wash with commercial soap containing shampoo	0.466
Step 3: Wash with commercial TEALS based shampoo	0.538

[a]Washing and rinsing in 100-ppm hardness water. Data provided in private communication by F. Schebecewe

melanization process with ageing. Nagase et al. [62] found that hair with a porous medulla gives a whitish appearance with less luster. These air spaces increase the scattering of light due to a change in refractive index at the hair to air interface creating a gray or whitish appearance. This effect is analogous to the one in the genetic abnormality of pili annulati or ringed hair. Pili annulati appears as bands or rings of silver or gray and dark regions along the axis. Musso [63] working with guidance from RDB Fraser observed that ringed hair contains bands or areas with air spaces in the cortex along the axis. These air spaces correspond to the silver or gray bands. The air spaces are believed to be caused by a defect in the synthesis of the microfibril-matrix complex in the cortex with less of it being produced. Therefore, cavities or air spaces are created in the hair [63]. So, gray hair with a porous medulla appears whiter than the same hair without a medulla.

10.6.6 Shampoos, Sebum, and Hair Shine

Schebece and Scott (private communication), using a light-scattering technique demonstrated that sebum de-lusters hair and soap-containing shampoos diminish hair shine. The soap effect can only be seen when hardness is present, but it can be detected in hardness as low as 100-ppm and lower (Table 10.9). Thompson and Mills [54] found a similar effect with soap-containing shampoos at 300-ppm hardness. More recently we found such effects with soap-containing shampoos at 60–80-ppm hardness.

The data of Table 10.9 show that sebum dulls hair and that soap deposits from shampoos also de-luster hair. Similar dulling effects may be observed after shampooing hair with a shampoo containing cationic polymer ingredients (Schebece and Scott, private communication). These deposits are often not uniform on the hair surface. Therefore, they can increase diffuse scattering; however, decreases in the specular component may also be seen with increasing deposition of some conditioning ingredients.

10.6.7 Hair Sprays Decrease the Shine of Single Hairs

Schebece and Scott (private communication) examined several commercial hair sprays for hair luster before and after soaking fibers in different concentrations of

the product concentrates. In all cases, the specular/diffuse reflectance ratios decreased (from 2% to 14%) depending on the concentration and type of resin used. Combing and other physical manipulations of the resin on the hair produced cracks in the hair spray resins, increasing the diffuse scattering and further dulling the hair. A method for hair assemblies is required to determine if the additional improvement in hair alignment by hair spray deposits will compensate for the increase in diffuse scattering.

10.6.8 Permanent Waves and Visual Assessment of Hair Shine

Dark brown hair tresses were treated with a commercial home wave and then visually assessed by panelists as slightly less shiny than the untreated control. A color shift to a slightly lighter shade was also noted. This shine change is believed to be due to an actual dulling of the fibers rather than to curvature or alignment changes.

10.6.9 Oxidation of Hair and Visual Assessment of Hair Shine

A group of five subjects were treated half-head-style with a surface oxidative treatment (diperisophthalic acid described in Chap. 5). This treatment oxidized the hair surface but did not penetrate to the cortex. Therefore, no pigment was oxidized and no color change occurred. Both subjects and independent observers through 1 month after treatment made shine evaluations. Independent observers all agreed that the treated side was less shiny than the untreated side. However, only one subject could detect this de-lustering effect on her own hair. These results suggest that oxidative treatments, including hair bleaches, dull hair. In addition, independent observers are more sensitive to hair shine changes on heads than self-evaluation of hair shine. Oxidative treatments that lighten the hair will decrease hair shine.

10.6.10 Abrasion of Hair Decreases Hair Shine

Schebece and Scott (private communication) abraded hair fibers against a smooth Bakelite surface in one experiment (Fig. 10.26) and against a 50-μm tungsten wire in another. The data show that surface abrasion decreases hair shine (specular/diffuse reflectance). This dulling effect increased with increasing abrasion. In certain instances, the total amount of reflected light and the specular component both increased. The specular/diffuse ratio always decreased. These results suggest that teasing (back-combing) hair and other abrasive actions such as vigorous

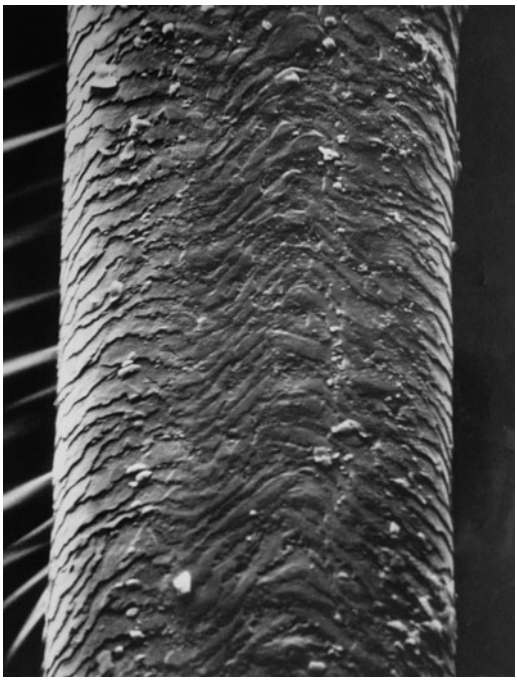

Fig. 10.26 Electron micrograph of a hair fiber mechanically abraded by rubbing against another hair. Note cuticle abrasion and hair fragments on the hair surface

combing or brushing can de-luster the hair by breaking scale edges and creating more irregularities on the fiber surface. These actions dull hair by increasing diffuse scattering.

10.7 Hair Body

10.7.1 Body Definition and its Relationship to Single Fiber Properties

Hair body is defined in the textile trade as that compact, soft, or firm-feel of textile stock or fabric [64]. It is a tactile property. With regard to human hair, body may be defined as thickness or apparent volume of a hair assembly, involving sight and touch for assessment [1]. The quality of liveliness or springiness [65] is also associated with hair body. Hough et al. [36] defined body as the structural strength and resiliency of a hair mass, which is consistent with the above definitions.

Body is a complex characteristic involving several single-fiber properties, including friction, stiffness, curvature, cross-sectional area or diameter, weight, and length (Table 10.10). If we consider changes instead of absolute values for hair body, it permits us to neglect properties that are not changed by cosmetic treatment

Table 10.10 How single fiber properties of hair relate to hair body [1, 2]

Increase in these fiber properties produces an increase in hair body	Increase in these fiber properties produces a decrease in hair body
Curvature[a]	Cohesion[a]
Friction	Weight
Stiffness	
Diameter	

Note: Fiber length is not considered, since it is not changed by cosmetic treatments
[a]Relatively large effect predicted

such as hair density on the scalp and fiber length. Thus considering changes by treatments simplifies the analysis. This approach suggests that if one makes the fibers stiffer, increases their diameter or curvature, or increases the frictional forces between the fibers, hair body will increase.

Hough et al. [36] used a slightly different approach and concluded that five groups of fundamental parameters govern hair body:

1. Hair density on the scalp
2. Stiffness
3. Diameter
4. Fiber interactions
5. Curvature

Thus, increasing hair density on the scalp, stiffness, diameter, or curvature increases hair body. For fiber interactions, the effects depend on the nature of the interactions. Obviously, these two independent approaches are related, and both lead to the conclusion that hair body can be studied systematically through single-fiber properties. However, if we consider only the changes that can be made to hair fibers by cosmetic treatments, then curvature has the greatest impact on hair body. Furthermore, if curvature is high it can dominate changes in hair body as it can for most consumer hair assembly properties as predicted by the C^2 hypothesis.

10.7.2 Methods to Evaluate Hair Body

Several laboratory methods have been described to characterize hair body [37, 67–76]. The Tolgyesi omega loop method [66] examines structural strength of a hair assembly, emphasizing the bending properties of an assembly more than the frictional properties of the fibers. One method that emphasizes frictional behavior but attempts to measure the bulk of hair fibers is the cylinder method of Scott and Robbins [69]. This method involves randomly dropping 1–2 in. hair fibers into a graduated cylinder. Fibers with higher inter-fiber friction tend to provide a larger volume and therefore more body.

The method of Clarke, Robbins and Reich uses image analysis to approximate the volume of hair tresses [72]. This is probably the best of all current hair body

methods. The Textile Research Institute's (TRI) method [68] involves transverse compression of a bundle of fibers to determine the compressibility and recovery behavior of hair tresses. Garcia and Wolfram [70] considered the force or work necessary to pull hair tresses through a Teflon ring. Here the net force is a combination of fiber bending and fiber-fiber and fiber-ring friction. But it is not clear with either of these two methods which parameter or combination of parameters correlates best with hair body. TRI suggests that their method is intended to measure the "tactile component of hair body as it is reflected in the resistance that hair offers to compression."

Another approach, by Robbins and Crawford [73], is a modification of the Garcia-Wolfram method. In this system, the bulk of a hair assembly is assessed by measuring the work required to pull the tress through a succession of very thin (0.076 cm) circular templates of decreasing diameter. A plot of work values vs. circle diameter is extrapolated to zero work to obtain the "maximum tress diameter." This parameter appears to be a measure of the bulk of hair assemblies. Dr. G. Blankenburg et al. (private communication) of the German Wool Research Institute has independently developed a similar method using this principle.

The Robbins and Crawford [73] method estimates the visual or volume component of hair body with some contribution from springiness or compressibility and resilience of the hair assembly. This measure of hair body shows that body increases with increasing amounts of hair, with increasing fiber curvature and with increasing inter-fiber friction.

Robbins and Crawford [73] examined hair of different curvatures by water setting Curl type II Caucasian hair in different configurations by curling hair tresses on glass rods and also by braiding hair tresses. They used the ratio of the coiled length of the hair to its extended length (Lc/Lt) as a measure of hair curvature. This ratio is the reciprocal of the natural to straight length described by Hardy [48] as a measure of hair curvature. As the number of braids increased the size of the braid pattern decreased providing a curlier-kinkier tress. The results showed that the larger number of smaller curls (curly to kinky hair) was more effective in producing hair body by this method than the larger curls.

Clarke, Robbins and Reich [72], questioned 150 panelists (Caucasian women and men) and found that only 15% of these consumers use the word stiff to describe hair body, but volume, bounce and thickness were used by 90 some percent of the panelists. This consumer research suggested that both visual and texture analysis are involved in hair body and that hair assembly volume is the primary factor in visual analysis by consumers.

To measure the visual component of hair body, Clarke et al. [72] evaluated four images of each tress by rotating the tress 90° for each image and comparing the results with images from a standard hair tress. Three types of hair were used, Asian, Caucasian and African American. All hair was made into tresses (1–6 g). The Asian and Caucasian hair was permanent waved to different degrees to provide a wide range of visually different tress volumes ranging from Curl type I to Curl type V. The initial results of measured tress volumes were compared with evaluations by panelists who visually estimated hair body.

The highly coiled African American hair (Curl type V) caused confusion among the Caucasian panelists, some judging these tresses to represent very little body while others rated them with very high body. Nevertheless, there was still a highly significant rank correlation (Rho = 0.865 and $p < 0.001$) between hair volume by image analysis and panelists visual rankings of hair body. However, when the data for the African American hair was excluded the correlation improved to Rho = 0.975 and $p < 0.001$. Unfortunately, a panel of African Americans was not assembled to determine if their perceptions would provide the same or a different result from that of the Caucasian panelists. Nevertheless, these experiments show that the volume component of hair body does increase with hair fiber curvature from Curl type I–IV when Caucasian perceptions are involved. Furthermore, the volume component of hair body increases with actual hair fiber curvature over the entire curvature scale.

Robbins [42] demonstrated that the cohesive effects of oils such as synthetic sebum have a "much greater impact" by substantially decreasing hair volume for wavy Curl type II hair than for high curvature Curl type V hair. The effect was relatively small for this curly type hair. From these experiments with cohesive oils on hair volume vs. curvature, Robbins concluded that at high curvatures the effect of fiber curvature on hair volume is dominant. It clearly has a greater impact than changes in other fiber properties such as cohesive forces, fiber friction or stiffness. Such dominance likely begins in Curl types IV and increases through curl Type VIII and is consistent with the C^2 hypothesis.

Dr. Hans Dietrich Weigmann (private communication) suggested from his work on compressibility and body of hair assemblies [68] that fiber curvature was the most important controlling property to their measurement of hair body. In addition, Dr. Mario Garcia (private communication) offered privately from his body method on hair compressibility and resiliency of tresses [70] that fiber curvature was clearly the most important fiber property to these important aspects of hair body. This work reinforces the hypothesis [6, 42] that at a high degree of curvature (curl type IV through VIII), curvature dominates most hair assembly properties, but at low curvatures it displays lesser effects.

10.7.3 Treatment Effects and Hair Body

Permanent waves and hair bleaches are known to increase hair body; however, the mechanisms of action of these products are different. Permanent waving increases hair body by increasing both fiber curvature and fiber friction [74, 75]. Both of these effects increase hair body (see Table 10.10). Bleaching hair does not increase hair fiber curvature, but it increases inter-fiber friction [75, 76].

On the other hand, creme rinses are purported to make curly to straight hair limp. Pomades are heavy leave-on oils that aid in combing and managing African type hair, but they do not make highly coiled African type hair limp. Limpness is the inverse of hair body. This effect is probably due to the fact that creme rinse

ingredients decrease inter-fiber friction [74, 75]. Some crème rinses display mild cohesive effects too, especially on low curvature, fine hair.

Conditioner sets are an interesting category, because some of these products increase hair body. At the same time, conditioner sets make hair comb easier. Such effects probably arise because these products reduce high-load friction when the hair is being combed wet (or even when dry). Upon drying, some conditioner sets increase low-load friction and or adhesive forces between fibers. Certain hair sprays behave in this same manner. Increases to the "apparent" fiber diameter are also possible for conditioner sets and hair sprays when they are well distributed throughout the hair.

Shampoos vary in their effects on hair body. High-cleaning shampoos increase the body of dirty (greasy) hair by removing oily soils. These effects decrease cohesive forces between fibers and increase inter-fiber friction. On the other hand, continued use of conditioning shampoos can lead to limp hair by reducing inter-fiber friction and increasing cohesive effects between hairs. These effects are similar to the action of creme rinses. This limpness effect is greatest for straight, fine hair and least for very curly to kinky hair.

10.8 Relative Scalp Coverage or Hair Amount

Robbins and Dawson et al. [7] described the effects of diameter and hair density (hair counts) on age and proposed a new metric "relative scalp coverage" for the perception of the amount of hair. This parameter or modification of it may ultimately find use for quantitation of the perception of the onset or different stages of female pattern alopecia and male pattern alopecia.

When considering only diameter and density this metric is defined as a two dimensional parameter as the average fiber cross-sectional area times the number of hair fibers per square centimeter. In its simplest form, when considering only diameter and density for female Caucasians, relative scalp coverage peaks at about age 35 [7]. This peak age is produced because hair diameter increases until about age 45 but density peaks in the late twenties. So, when these two important contributors to scalp coverage are combined, they provide a maximum for relative scalp coverage for Caucasian females at age 35. The average age for relative scalp coverage for males would be lower, likely in the twenties, since hair diameter for males peaks at about twenty and hair density if it is similar to females peaks in the late twenties.

Robbins and Dawson et al. proposed that when other important fiber parameters are considered for relative scalp coverage, it will have to be considered as a multi dimensional system involving diameter, density, fiber curvature, fiber length, color (hair and scalp) and style and it can relate very much to a hair body metric. Since Mirmirami and Dawson [77] have shown scalp site produces different effects on diameter and density, scalp site will also have to be considered for a more complete model.

10.9 Style Retention

10.9.1 Style Retention Definition and its Relationship to Single Fiber Properties

Style retention may be defined as the ability of hair to stay in place after styling [1]. It is time-dependent and includes curl retention, wave retention, and straightness retention. Style retention may be described in terms of single-fiber properties or it may be treated as an assembly property. Style retention is most important to many hair products including permanent waves and hair sprays as well as to conditioner sets or wave sets, setting gels and to mousses.

When a hair fiber is thoroughly wet with water and allowed to dry it will gradually revert to its natural curvature. For example, a curly hair will assume a curly or coiled configuration, whereas a straight hair fiber will assume a straight configuration. This property of hair fibers to assume their natural curvature is central to the STAM method for curvature assignment [35, 78, 79]. If hair is wet with water and held and dried in a pattern different than its natural curvature it will tend to remain in that configuration until rewet or exposed to a different relative humidity. This type of action is the basis of water setting human hair.

Some heating devices such as blow dryers or hot air straighteners or curling devices are sometimes used to speed up the drying process and to facilitate styling by way of a water set. These devices provide only temporary effects because the primary bonds that help hold the hair in this type of water set configuration are hydrogen bonds and they can be broken by water or exposure to changes in humidity whereupon the hair fiber reverts to its natural curvature.

It has been known for years that exposing water set hair to higher humidity causes the hair to revert to its natural curvature and the water set decreases. Diaz et al. [80] demonstrated that exposure of a tress of water set hair to a lower humidity can also produce a loss of water set. Robbins and Reich [81] showed that water setting single hair fibers into a coiled configuration at 60% RH and then exposure to 10% RH produces a greater loss in style retention than similar single hairs water set and held at 60% RH. The use of single hairs in this experiment demonstrates that this effect is solely an effect of water on the curvature (internal bonding) of the hair fibers and does not involve inter-fiber friction. These results show that *changes in RH* are detrimental to water set in human hair fibers and it is not just exposure to higher humidity.

Therefore the transfer of water into (higher RH) or out (lower RH) of the hair fiber results in breaking hydrogen bonds that are involved in a water set and such an action produces a loss in the water set. As with other hair assembly properties, style retention can be dominated by hair fiber curvature [6, 42]. Confirmation of this conclusion is the fact if a person with high curvature hair (Curl type IV–VIII) wishes to wear a straight type hair style that type of style is difficult to achieve with a water set. However, if a person with straight hair, for example, Curl type I or II wishes to wear a curly hair style, to a limited degree, this can be done with a water set supplemented by hair sprays.

Table 10.11 How single fiber properties of hair relate to style retention [1]

Increase in these fiber properties produces a decrease in style retention	Increase in these fiber properties produces an increase in style retention
Curvature[a]	Friction (low load)
Stiffness	Cohesion
Weight[b]	Curvature[a]

[a]A curvature increase can increase or decrease style retention (see text)
[b]Only for curly to wavy hair styles. For straight styles increasing weight increases style retention

However, making the natural curvature consistent with the optimum curvature for the desired style is the best way to achieve these effects. There are permanent, semi-permanent and short term treatments to achieve this type of goal. For curly hair styles reductive permanent waves are semi-permanent treatments. With the proper size and shape curlers these treatments can provide coiled hair from relatively straight hair in a semi-permanent manner. Furthermore, a permanent wave provides better style retention for a highly coiled style from straight hair than by water setting because for such a style the most important property is hair fiber curvature. The same applies for providing a relatively straight hair style from highly coiled hair. Furthermore, providing for straight hair styles from highly coiled hair, the only permanent treatments are alkaline straighteners. The more important fiber properties that are related to style retention are curvature, friction, stiffness, cohesion, and weight [1, 2]. Table 10.11 suggests that increasing fiber stiffness and weight will decrease style retention. However, for straight hair styles, increasing weight improves style retention. The role of weight is straightforward; that of stiffness is more subtle. Hair fibers are generally water-set to produce an optimum curvature for the desired style. The desired style sometimes differs from the natural curvature of the hair. Changes in humidity promote deterioration of the water set and a gradual change toward the hair's natural curvature [81]. Only friction and cohesive forces tend to hold the assembly in the desired style preventing the hair from reverting to its natural curvature. The stiffer the fibers, the more readily they tend to overcome these frictional forces and the desired style. Thus, increasing fiber stiffness decreases style retention for water set hair.

The maximum fiber curvature consistent with the desired style will produce the optimum number of entanglements and the optimum fiber-fiber interactions and thus the maximum style retention. Generally, an increase in fiber curvature increases style retention. However, if the desired style is considerably straighter than the natural curvature, then a decrease in fiber curvature will be necessary to improve style retention (hair straighteners or relaxers). The converse holds for styles that are curlier than the natural curvature of the hair.

10.9.2 Methods Relevant to Style Retention

Most companies involved in hair products have developed their own procedures for evaluating curl or wave retention of hair assemblies (tresses, wigs, or heads).

Laboratory procedures also vary, depending on the type of product to be evaluated. Differences in application of hair sprays and permanent waves and the difference in performance characteristics require different procedures. The extent of quantitation may also vary. For example, Reed [82] described the evaluation of permanent-waving agents by simply treating tresses wound on curlers and qualitative evaluation of the hair for "curl strength" after removal from the curlers. Other, more quantitative approaches involve calculation of percent curl retention [83] or percent waving efficiency or measuring curl strength [84–86].

Basically, curl retention procedures involve treatment of a tress of known length, winding it on a mandrel or a rod or around pegs, and drying or conditioning it. After removing the hair from the rod, either length measurements vs. time (under controlled humidity) are taken to arrive at percent curl retention. Alternatively, the hair is placed on water and the change in elongation provides a means to obtain percent waving efficiency for cold wave lotions [84, 85].

The curl strength method of Stravrakas et al. [86] is an interesting option. This method involves treating hair, curling it on rods, conditioning it at high humidity. The researcher then determines the resistance to the deformation of curls and waves by the hair treatment using an Instron tensile tester or another strain gauge device. This method provides a large variance; however, it can distinguish between cold waves, hair sprays, and water-set hair.

For hair sprays or hair fixatives, several techniques have been described to evaluate curl-holding ability under conditions of controlled humidity [87, 88]. One novel approach [88] involves the rate of untwisting of tresses treated with the hair fixative. This method correlates with curl retention tests, yet it allows for faster evaluation of treatments.

Robbins [89] used a single fiber method for determining curl retention or straightening. This method offers advantages when used in conjunction with a fiber assembly method (tress method), since it eliminates fiber-fiber interactions from curvature and stiffness changes. It consists of uniformly winding a single hair fiber of known length onto a glass rod, treating it with water or product, and conditioning the hair at a controlled humidity (generally 50–65% RH). The fiber is then removed from the rod and conditioned at different RH's. Changes in length with time are measured with a cathetometer. See Chap. 4 for a discussion of some of the results with this method regarding water setting hair.

10.9.3 Style Retention and Hair Treatments

Permanent waving or relaxing of hair improve style retention when the degree of curl is made more consistent with the desired hair style. Obviously, the type and size of rollers (curlers) in permanent waving are important in determining the final result. The roller dimensions should be consistent with the curvature required by the desired hairstyle. Permanent waving increases inter-fiber friction [75] which also contributes to improve style retention, especially low load friction.

Bleaching increases inter-fiber friction [75, 76] which helps to improve style retention. Most conditioner or creme rinse ingredients [76], in contrast to bleaches, provide a decrease in inter-fiber friction. Except for some straight hair styles, many hair conditioners decrease style retention.

Conditioner sets, setting lotions, mousses, and hair sprays all increase low load inter-fiber attractive forces that help to improve style retention. These effects are greater than that of the weight increase by these ingredients which in some cases tend to decrease style retention.

Cleaning shampoos, when used on hair containing sebaceous soil, remove the surface oils and thereby reduce the cohesive bonding between fibers. These products thus provide an improvement in style retention for "dry look" hair styles. Certain conditioning shampoos provide a decrease in fiber friction and an increase in cohesive bonding. In that manner, they provide for a limp look and a decrease in style retention for many hair styles.

10.10 Hair Manageability

10.10.1 Hair Manageability Definition and Single Fiber Properties

As defined earlier, manageability is the ease of arranging hair in place and its temporary ability to stay in place; long-term effects on hair fiber assemblies are not considered for this property. Manageability is such an inclusive term that it cannot be measured by one single procedure.

As indicated earlier, Robbins et al. [4] concluded that three properties were strongly and significantly associated with manageability: easier combing, reducing static flyaway and keeping hair in place during styling operations. Garcia and Diaz [9] even earlier pointed out that "combability is closely associated with manageability" and Mills, Ester and Henkin [43] referred to the importance of static charge and flyaway hair to manageability.

Robbins et al. [4] found that manageability was perceived differently by different persons and by different hair types. They proposed that hair type and the desired hair style were critically important to the manageability properties expected by consumers. Furthermore, the "curvature of a hair type is obviously associated with the degree of curliness of a hair style and is perhaps the most important of these" three properties. They suggested that when the hair type, curvature, length and texture of the hair match the desired hair style, manageability problems are minimized. However, when the hair type does not match the desired hair style then manageability problems are maximized.

Since combing ease, flyaway hair and style retention (short term, i.e. during styling) are all components of hair manageability and because these three hair assembly properties are all dominated by curvature the logical conclusion is that

fiber curvature dominates many manageability issues. For example, when curvature is high and it matches the desired hair style then manageability will be concerned primarily with combing or picking the hair to the desired style. In that situation, style retention concerns will be minimized, and flyaway hair will be of concern primarily for straight to wavy hair but not for very curly hair. However, when the curvature is low and a high curvature hair style is desired then style retention concerns will be higher. So, the further the natural curvature of the hair is from the optimum curvature of the desired style the greater the issues with style retention manageability. The closer the natural curvature is to the desired style the fewer issues with style retention and the more issues with combing/brushing/picking or with flyaway hair; however, flyaway hair is not an issue with high curvature hair such as Curl types IV–VIII, but becomes more of an issue as the natural curvature of the hair decreases.

Therefore to enable a quantitative approach to manageability, Robbins et al. [4] recommended considering this important cosmetic property in terms of its component assembly properties that can be readily visualized and measured. So, manageability is concerned with:

Arranging hair in place (combing/brushing),
Keeping hair in place (style retention during styling), and
Flyaway hair.

Therefore, the suggestion was made [4] to consider these three types of manageability to permit measurement and scientific evaluation, rather than the single elusive term manageability:

Style arrangement manageability (combing/brushing/picking),
Style retention manageability (style retention when styling), and
Flyaway hair manageability.

Existing tests to evaluate hair-combing ease, style retention, and flyaway hair or static charge may then be used to evaluate these different types of manageability. Furthermore, each type of manageability may be expressed in terms of a ratio of control/treatment values.

Using this approach, those single fiber properties defined in Table 10.11 that improve combing ease will also improve style arrangement manageability, while those properties of Table 10.11 that improve style retention will improve style retention manageability. Similarly, those parameters described in the previous section, which decrease static charge on hair, will improve flyaway hair manageability and thereby decrease static ballooning.

Therefore, increasing fiber curvature, static charge, or high-load friction will decrease style arrangement manageability. On the other hand, increasing low-load friction or cohesive forces between fibers will improve style retention manageability. This means that a change in fiber curvature can either increase or decrease style retention manageability. For example, if the treatment changes the curvature so that it is either too straight or too curly for the desired style, it will make the hair less manageable. However, if the treatment makes the hair curvature more consistent with

the desired style, then that type of change will improve style retention manageability. Since fiber length is not changed by cosmetic treatments, length is not relevant for this type of analysis which considers changes by cosmetic treatments.

10.10.2 Treatment Effects and Hair Manageability

Since style arrangement manageability and style retention manageability often oppose each other, the decision as to whether a given effect will improve manageability for any particular person's hair depends on which of these two components of manageability is desired more. Since different persons will attach different values to the three different types of manageability, it is very difficult to predict overall manageability. Moreover, it is preferable to discuss each of the three types of manageability separately rather than to try to arrive at a composite for this important cosmetic property.

Permanent waving can increase style retention manageability when it provides an amount of fiber curvature that is more consistent with the desired hair style. Permanent waving also increases low-load friction, thus improving style retention manageability. Permanent waves are generally used to increase fiber curvature, thereby increasing the number of possible entanglements and decreasing style arrangement manageability. Increasing fiber friction also decreases style arrangement ease. Most satisfied users of permanent waves are more concerned with the staying in place component of style retention manageability. Therefore, they feel that after a permanent wave, their hair is more manageable. Those dissatisfied with the style arrangement manageability of a permanent wave can decrease fiber friction with a conditioner and thereby improve style arrangement manageability.

Most conditioner ingredients decrease high-load friction [50, 76], thus making the hair comb easier thereby improving style arrangement manageability. At the same time, quaternary conditioner ingredients decrease fiber chargeability. This latter effect, in combination with combing ease, decreases the propensity of the fibers to fly away and thus improves flyaway manageability. Most satisfied users of conditioners are more concerned with style arrangement and flyaway manageability than with style retention manageability. Therefore, they conclude that their hair is more manageable after using a conditioner. Pomades provide a decrease in high load friction and an increase in cohesive forces between fibers. Those satisfied users of pomades generally have high curvature hair and are satisfied with high curvature hair styles. Therefore, these consumers do not have concerns with style retention manageability, but are more concerned with style arrangement manageability which is delivered better with pomade products than with ordinary rinse-off hair conditioners.

Satisfied users of conditioner sets, setting lotions, pomades, and hair sprays are generally more concerned with style retention manageability. Therefore, the increase in inter-fiber cohesive forces from these products more than offsets any decrease in style arrangement manageability concerns.

High-cleaning shampoos remove sebaceous oils and decrease cohesive forces between the fibers, thereby making the hair more conducive to "dry look" hair styles. These products increase frictional forces relative to dirty hair. These effects aid style retention manageability for "dry look" styles. Satisfied users of these shampoos, who do not use other hair products, are generally more concerned with these factors (related to how hair stays in place) than with style arrangement manageability. Users of high-cleaning shampoos plus conditioners or high-conditioning shampoos are generally very concerned with improving style arrangement manageability and flyaway manageability for a "dry look" type of hair style.

10.11 Hair Handle or Feel

Tactile properties of hair fiber assemblies such as softness, smoothness and moisturization are important to advertising of hair products. But tactile properties provide difficulty in assessment in and between different laboratories. Boucsein et al. [90] described that the use of psycho-physiological techniques aided discrimination of sensory assessments. For example measurement of peripheral blood volume and facial muscular activity were found to be more sensitive and discriminating than ordinary sensory assessment to effects and interactions between emotional and technical responses to three different hair samples including two different shampoos and one untreated control.

Wortmann and Schwan-Jonczyk [91] working with a European Hair Products Group conducted a study to determine how single fiber and hair collective properties contribute to hair feel or handle. From a study on 4 hair types of European hair braids, the bending properties of single fibers interacting in the tress as a fiber collective and fiber friction were found to be the most important fiber properties related to handle. Single fiber friction was determined by a capstan method on root, middle and tip sections of hairs. Significant differences between hair types were found for diameters, ellipticity, bending stiffness and friction. Handle or feel was perceived as inferior when the hair was coarse and the bending stiffness was high. Friction was also important to feel especially in the tip regions of the hair. Hair perceived as fine was soft and friction appeared to play less of a role than in hair perceived as coarse.

Kawasoe et al. [92] added to these findings by showing that an increase in hair fiber friction produces the perception of a more coarse texture for hair. Alteration of the hair surface by damaging treatments generally produces an increase in hair fiber friction resulting in what is perceived as a more coarse texture for hair. Kawasoe et al. determined that hair damage is perceived as a more irregular or more varied scale pattern (as opposed to uniform but different scale heights and widths). This conclusion came from having consumers feel simulated cuticle structures on an artificial hair surface of engraved images of different scale patterns on polyimide plates. A highly varied or irregular scale pattern produced what is perceived as a coarse texture for hair.

This conclusion is related to results of unpublished work where we bleached hair to different extents and had blindfolded female panelists evaluate hair tresses. The hair was rated for coarseness and tested for friction. The greater the degree of bleach damage, the higher the friction and the more coarse the ratings.

We know that African type hair is elliptical, highly coiled, and larger in diameter than Caucasian hair. It is also generally perceived and described as coarse hair. Asian hair on the other hand is the largest in diameter of the three major geo-racial groups and it is the least coiled, the most circular and is usually characterized as straight and coarse. However, quantitative studies by Nagase et al. [3] on the curvature of hair fibers from 230 Japanese women showed that about 53% of Japanese women have straight hair and 47% have hair that varies from slightly wavy to what is perceived as frizzy. As indicated earlier, the peak in the distribution for curvature was at Curl type II and extended to Curl type IV on the STAM curvature scale. Frizzy Japanese hair is distinguished from curly hair by neighboring hairs not being parallel or synchronized [3].

These scientists concluded that there should be a positive correlation between hair fiber curvature and the perception of coarse hair, a reasonable conclusion. However, I could not find data in the literature to either support or deny this conclusion. This is an area that requires additional research.

10.12 How Consumer Hair Assembly Properties Change with Age

Considering one variable at a time, it is easy to qualitatively predict the changes in Consumer Hair Assembly Properties (CHAP) with respect to age; however, unfortunately changes in hair properties with age do not happen one variable at a time. In this section, we will discuss different stages of life considering the aggregate and/or individual changes in hair fiber properties and how these affect the CHAP in terms of the following five stages in the life of hair fibers:

Infancy to childhood: approximately the first year of life.
Childhood to puberty: about age 1–12.
Puberty to young adult: about age 13–30.
Young adult to middle age: about 31–45.
Middle age to and including advanced age: approximately 45 and upward.

10.12.1 Infancy to Childhood: Approximately the First Year of Life

Infants hair is very fine [93–95] (about 30 μm in diameter for infants, about 60 μm for children and somewhat larger but highly variable for adult Caucasians). These

average fiber diameters tell us that the time-span of anagen (growth period) for infants' hair is shortest compared with children or adults until about age 20 (for males) and middle to advanced age (about 45 for females) when anagen starts to become shorter once again. Infants' hair was found to be less elliptical (1.26 vs. about 1.37) in one study of Caucasian infants vs. children's hair and about 1.38 for adult Caucasians. So, the hair of infant Caucasians is more round than children's [93] or adults hair.

The fine hair of infants is lost by about the seventh month and is replaced by a coarser and longer hair which is generally replaced by an even coarser hair at about 2–3 years of age [95]. The loss of hair tends to be randomly dispersed over the scalp; however, during infancy, Pecoraro et al. [94] suggested that the initial hair loss may occur in waves. Infants' hair grows to only about 15 cm long compared with the final stage of children's hair that can grow to about 60 cm and adults hair can grow even longer to about 100 cm see Chap. 1.

Hair lipids are produced by two sources, the sebaceous glands, located in each hair follicle and the hair matrix cells that produce the growing hair fiber. The cholesterol level of forehead skin is low at birth, but it reaches a maximum at about age 6. It then declines to near adult levels by age 9 [96]. Cholesterol is produced primarily by the hair matrix cells and since sebum production is low in infants and children, the cholesterol level in human hair fibers is high during infancy and childhood when sebaceous lipids are low. Therefore, fine hair of Caucasian children tends to provide low hair body and is generally easy to comb unless it is curly.

I could not find data on hair density of infants, but sources state that follicle density is highest in the fetus and it decreases with increasing skin surface accompanying growth of the head. Estimates of the scalp surface area of adults are about 350–400 cm^2, while that of infants at birth would be approximately 200–225 cm^2. These scalp areas are approximate dimensions of the head of infants vs. adults calculated from head dimensions found in the Merck Manuals Online Medical Library [97]. Assuming a follicle density of about 321 follicles/cm^2 for Caucasian adults [98] and assuming the only change is the surface area of skin by growth, provides a scalp follicle density for Caucasians of 565/cm^2 at birth. Based on data by Sperling [98] for African Americans the follicle densities would be lower for that group and even lower for Asians from data by Tajima et al. [99].

10.12.2 Childhood to Puberty: Approximately Age 1–12

During childhood, scalp hair fiber diameter nearly doubles and the maximum length that the hair can grow to increases nearly fourfold from infancy to the first few years of childhood. However, fiber ellipticity increases only a small amount in Caucasians from infancy to childhood [93]. This ellipticity effect is likely not

meaningful in terms of CHAP. I could find no literature on the hair curvature changes during this time period. There may be changes in hair color during this time period.

The large increase in hair fiber diameter from infancy will increase tensile and bending stiffness but torsional resistance of hair fibers will decrease. Unless there is a noticeable increase in hair fiber curvature, the stiffness increase will add body to the hair, making it fuller. The stiffness factor alone will tend to make the hair comb easier. The hair fiber diameter and length increases are due to longer anagen periods and are clearly the most important changes (unless there is a large curvature change) in terms of hair body, style retention, etc.

Hair tends to be relatively dry during childhood because of the low sebaceous output [100, 101] with the composition of the hair lipids being high in cholesterol [102] and its esters while the percentages of squalene [102] and fatty acids [103] are lower than in the hair of teenagers or adults.

10.12.3 Puberty to Young Adult: Approximately Age 12–30

During this stage there is approximately a 25% increase in scalp hair diameter and an increase of about 60% in the maximum length that the scalp hair fiber can achieve. The anagen period is frequently as long as 6 years during this phase of life compared to about 2–4 years in the previous stage. The diameter increase for males tends to peak near the late teenage years, however, for females it continues through this stage and into the next. Once again the most important missing information in terms of hair behavior is the lack of data on changes in hair fiber curvature. Nevertheless, an increase in curvature of the hair of Japanese females has been shown to occur from age 10 to 70 [104], but it appears to be a small and gradual increase that appears to be a bit larger in advanced years. However, we cannot even speculate as to whether this effect is sufficient to affect the CHAP, therefore this is a major gap in the hair fiber literature. I would expect a similar change in Caucasians hair too, although there is currently no evidence to support this conclusion at this time.

The beginnings of male pattern alopecia (MPA) can initiate during the middle part of this stage (about ages 19 or 20) for some Caucasian males, but it is normally a few years later for some Asians [105] and those of African descent, see Chap. 1. Female pattern alopecia (FPA) can initiate during the last part (late 20s) of this period (see Chap. 1 and references [108, 109]) and it tends to begin earlier for Caucasians than for Asians. Both of these conditions produce a decrease in the hair density (hair counts), but in spite of the decrease in hair density the average hair diameters continue to increase for females, but decreases for males during this stage [108–110]. By about age 30, MPA affects about 25% of Caucasian males see Chap. 1 and reference [105], but only about 5% of Asian males and most of those Asians are in the early stages of MPA.

During this stage, FPA affects only about 8% of Caucasian women, but it affects virtually no Asian women as shown by Norwood [106] and Birch et al. [107] for Caucasians and Chap. 1 for Caucasians and Asians. FPA occurs more in the top central part of the scalp and is more diffuse than MPA which initiates and tends to concentrate more in the frontal and crown areas. The increase in hair fiber diameter during this stage will increase tensile and bending stiffness, but it will decrease torsional resistance of hair fibers. These diameter and stiffness changes will tend to increase hair body and to make the hair comb easier [2].

There is a noticeable increase in hair greasiness for most persons during this stage [100, 101]. The greasiness effect is caused by both an increase in the amount and the composition of hair lipids. For example, the sebaceous lipids including squalene [102] and most fatty acids [103] and wax esters [101] increase in the hair while those lipids that are produced in the matrix cells in the hair follicle including cholesterol [102] and its esters decrease on and in the fiber.

These lipid changes (alone) at the hair surface tend to decrease hair body and require more frequent shampooing to improve the overall appearance of the hair in terms of hair matting and luster. For those with little or no MPA or FPA, the effects of hair diameter, stiffness and surface lipid deposits are the most important changes that occur during the first few years of this stage. This conclusion assumes that there are no changes in hair fiber curvature during this stage. Increases in hair fiber diameter and stiffness will tend to increase hair body and combing ease. For those with noticeable MPA or FPA, regional changes in hair density and fiber diameter especially during the latter part of this stage will tend to decrease hair body and combing forces.

The graying process initiates for some especially during the last decade of this period. Therefore, hair color can change during the last 10 years of this period. A few gray hairs are noticed at about age 21–22 for dark haired Caucasians, at about age 25 for Caucasians with medium colored hair and at about age 26 for fair haired Caucasians. By the age of 30 about one fourth of all Caucasians will have a small amount of gray hairs [111, 112], while about 20% of Asians and 15% of African descent will have begun graying [113].

10.12.4 Young Adult to Middle Age: Approximately 31–45

Hair density per unit area tends to gradually decrease during this stage [7, 77, 107] even for those with no noticeable MPA or FPA. This decrease in hair density should be more rapid and more scalp-region specific for MPA than for FPA and it occurs at a faster rate in the frontal and crown sites for males. Nevertheless this effect is still region specificity with regard to hair count decreases with age for women [77] and most likely for men too.

At the beginning of this period, only about 8% of female Caucasians have clinically observable hair loss, but at the end of this time period that number nearly doubles [106, 107]. The average hair density decrease for women not suffering

from FPA is about 26 hair fibers/cm^2 per decade or approximately 15% hair loss during this period which is generally not detectable. Data from Birch et al. [107] on two groups of women one group concerned about FPA and the other group not concerned with FPA suggests that a 30% hair density decrease is borderline detectable. Therefore, it would appear that the hair loss in FPA must be about two times this rate of hair loss over this same time period for some persons to be concerned about FPA. This effect is likely due to the increase in hair diameter during this stage for women.

The subjective impression of alopecia among females is multi-factorial involving hair density, hair fiber diameter and the often overlooked property of fiber curvature. A 25–30% decrease in hair density is borderline detectable. If most of the fibers are fine and straight the hair loss will likely be more noticeable than if the fibers are coarse and curly. The use of the new metric for relative hair coverage by Robbins and Dawson et al. [7] should become useful in improving our understanding of the perception of alopecia.

At the beginning of this life period our data suggest that about one-fourth of Caucasian men have Type II–VII (see Chap. 1, Table 1.5 and Fig. 1.12) hair loss, while only about 6% have Type V–VII (see Chap. 1, Table 1.5 and Fig. 1.12) hair loss. At the end of this stage about 46% of Caucasian men have Type III–VII hair loss and about 14% have type V–VII hair loss see Chap. 1 and references [107, 114–116]. On the other hand, less than 5% of Asian men have Type III–VII hair loss at the beginning of this period and about 12% have this same amount of hair loss at the end of this stage [115, 116]. I could not find data for those of African descent.

Approximately 5% of all Caucasians will be totally gray at the end of this period while virtually no Asians or those of African descent will be totally gray during this stage [111, 112]. A little more than three fourth of all Caucasians, about two-third of all Asians and by deduction about ½ of African descent will have some gray hair by the end of this period [111–113].

According to our sources on hair diameters vs. age, for females diameters gradually increase up to the end of this stage [108–110], but for males diameters continue to decrease [110]. Based on graphical data of smaller numbers of Caucasians [108, 109] I assume that a similar effect occurs for Caucasians and likely for those of African descent; however, I could not find sufficient data to estimate quantitatively the extent of those changes for these geo-racial groups.

The decrease in hair fiber diameter from the late teenage years upward for males will decrease tensile and bending stiffness but increase torsional resistance of hairs, while the continued increase in diameter for females will increase tensile and bending stiffness. Males will also suffer larger regional decreases in hair density/unit area and therefore will suffer a greater loss in hair coverage and hair volume and other evaluations of hair body from the diametric decrease. It is unfortunate that we know so little about hair fiber curvature changes with respect to age, however, there is one study that shows that the hair of Japanese women increases in curvature from age 10 through 70. However, there is no data for Caucasians or Asians on hair curvature vs. age. Lipid levels do not appear to change to a large degree for most Caucasians during this stage [100, 101].

10.12.5 Middle Age to and Including Advanced Age: Approximately 45 and Up

The primary effects of a decrease in hair density and in fiber diameter over multiple regions of the scalp in MPA will continue from the previous stage [117] and will worsen during this stage. The percentage of male Caucasians suffering from MPA increases during this time period from about 46% to about 70% see Chap. 1 and reference [105]. Related effects will occur with those suffering from FPA during this stage because both hair density and diameter decrease during this stage. The incidence of FPA in Caucasians is approximately 16% of women at the beginning of this stage and that percentage will double by age 75 see Chap. 1 and these references [106, 107].

Graying will further increase during this stage. Approximately 21% of Caucasians will go from little gray to moderate gray and about 35–40% more Caucasians will become totally gray during this time period see Chap. 1 and these two references [111, 112]. Using the Tobin and Paus approximation [116]; approximately 15% Asians and 10% of African descent will go from little gray to moderate gray, about 30% Asians will become totally gray and about 25% of African descent will go totally gray during this time period.

Major effects occur during and a few years prior to Menopause to the scalp hair of women including lower frontal scalp hair density [77] (on the frontal but not occipital scalp), lower growth rates [77], lower hair fiber diameters [77] and changes in the composition of hair lipids on and in the fibers [100–102, 118]. Lower total sebum in post-menopausal women vs. pre-menopausal women also occurs [100, 101].

These changes in hair effects translate collectively into lower hair greasiness and less softness and smoothness for post-menopausal women [118], and although there is a decline in lipid levels for males it is substantially less than for females [100, 101]. The hair of post-menopausal women has also been shown to be less shiny than the hair of pre-menopausal women [118]. Whether this decrease in hair shine is due to a decrease in fiber alignment from an increase in hair fiber curvature as occurs with age in the hair of Japanese women [104] or to another factor is not known. I would expect an increase in fiber curvature would also produce less synchronized waves or curl patterns with the end result being an increase in hair frizziness [104].

For males, the major effect during this stage appears to be a decrease both in hair fiber diameter and density. We know that this effect occurs in all geo-racial populations, but the relative quantitative effects need to be determined. The decrease in hair fiber diameter will decrease tensile and bending stiffness and increase torsional resistance of hair fibers. The effects on fiber diameter in combination with hair density produces a decrease in relative hair coverage in the frontal, parietal and crown areas of Caucasians and should produce changes in important consumer assessments such as a decrease in hair body and a reduction in combing forces which should be more apparent for men than for women.

For women the regional decreases in fiber diameter and hair density is generally less than for men, however there can be a meaningful decrease in hair density for women in the frontal and top central region of the scalp. In addition, the decrease in hair greasiness that would appear after a day or two or longer will tend to partly offset the decrease in hair body from a decrease in fiber diameter and stiffness for women except for the everyday shampooer. I would anticipate related effects on combing ease, that is, the decrease in stiffness will tend to make the hair more difficult to comb [2]; however the decrease in hair density will tend to make the hair comb easier. I would guess that the hair density effect would be larger, however which effect is stronger is too difficult to say without additional data.

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Appendix

Physicochemical Constants

0° C = 273.16 K
R gas constant = 1.987 cal deg^{-1} $mole^{-1}$
Standard gravity = 980.66 cm sec^{-2}; 9.8066 N/Kg
Faraday's constant = f = 23,062 cal (volt equivalent)$^{-1}$
Avogadro's constant = N = 6.0238×10^{23} molecules $mole^{-1}$
Density of hair = 1.32 g cm^{-3}
Refractive index of hair:
Epsilon = 1.56 (light parallel to fiber axis)
Omega = 1.55 (light perpendicular to fiber axis)
Elastic moduli at 60–65% RH for Caucasian hair:
Stretching = 3.89×10^{10} dyn/cm^2 = 3,890 MPa
Bending = 3.79×10^{10} dyn/cm^2 = 3,790 MPa
Torsion = 0.89×10^{10} dyn/cm^2 = 890 MPa[a]

[a]Bogaty HJ (1967) J Soc Cosmet Chem 18:575

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Approximate Diameter of a Few Keratin fibers

Fiber type	Diameter (μm)
Human scalp hair	
Terminal hair	30–120 (See Chap. 9)
Vellus hair	<4
Wool fiber	
Fine wool	17–33[a]
Coarse wool	33–42[a]
Horse hair	
Mane	50–150[a]
Tail	75–280[a]
Cat whisker	~450
Porcupine quill	can be >1,000

[a]Harris M (ed) (1954) Harris handbook of textile fibers. Harris Research Labs., Washington, DC

Units of Linear Measure

Unit	Symbol	Quantity
Meter	m	–
Centimeter	cm	10^{-2} m
Millimeter	mm	10^{-3} m
Micrometer	μm	10^{-6} m
Nanometer	nm	10^{-9} m
Angstrom	Å	10^{-10} m
Picometer	pm	10^{-12} m

Meter is the arbitrarily chosen standard of length of the metric system. It is the distance between two marks on a platinum-iridium bar kept at constant temperature at the International Bureau of Weights and Measures near Paris. For conversion to the English system, 1 m equals 39.37 in. and 1 cm equals 0.3937 in. (2.5401 cm = 1 in.), etc.

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