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

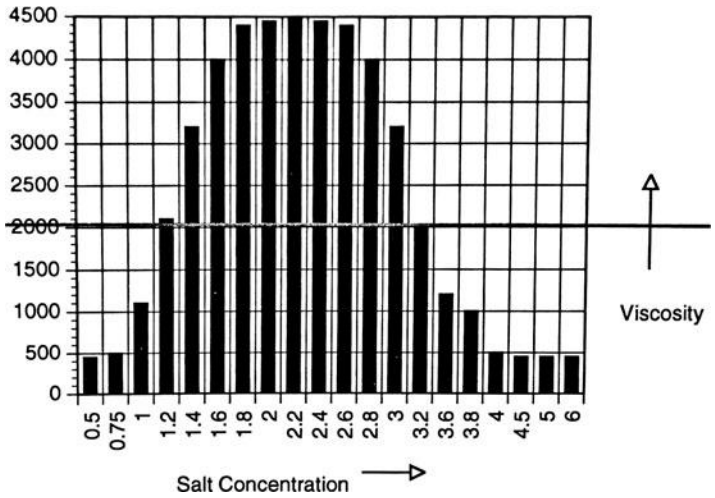


Fig. 6.1 The general relationship of the salt content to the viscosity in surfactant systems (shampoos)

carefully controlled to obtain the appropriate viscosity when salt control is employed.

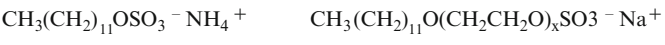
Polymeric gums such as methyl cellulose or hydroxy ethyl cellulose have also been used in shampoos to help control viscosity. Here, the polymers interact with the surfactants forming even larger more cohesive aggregates of higher viscosity. Alkanolamides interact similarly and are very effective in reducing 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

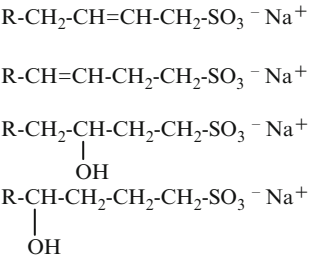
The main primary surfactant used in the United States for shampoos is ammonium lauryl sulfate, while in many other countries, sodium or ammonium laureth sulfate (with an average of 2 or 3 moles of ethylene oxide) is the current leader. These two surfactants are used alone or blended together for shampoos 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.

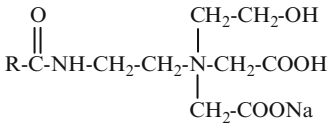
Baby shampoos (Table 6.4) and some light conditioning shampoos employ nonionic surfactants such as PEG-80 sorbitan laurate, PEG-20 sorbitan laurate or PEG-20 sorbitan oleate as the primary surfactant and amphoteric surfactants such as cocoamphocarboxyglycinate or cocoamidopropylhydroxysultaine are used 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

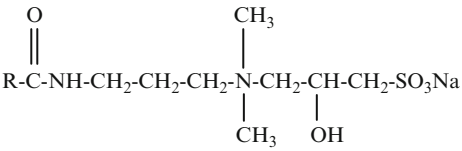
Ingredient	Percentage
Sodium laureth sulfate	8
Sodium lauryl sulfate	7
Cocamide MEA	2
Cocamidopropyl betaine	2
Glycerin	1
Fragrance	0.7
Citric acid	To desired pH
Sodium citrate	~0.2
Sodium chloride	To desired viscosity
Colors	To desired color
Sodium benzoate	As needed
Tetrasodium EDTA	As needed
Preservative (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:

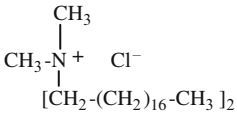
1. Dissolve the water soluble ingredients in deionized water while stirring and heat if necessary. This is part A.
2. If necessary, heat the oil soluble components to melt the solids. These ingredients may be added together or separately. The order of addition is often critical. This is Part B. When 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.

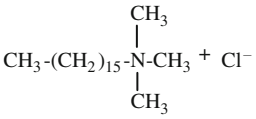
This discussion is obviously a cursory introduction into shampoo and conditioner making procedures. For more details on emulsions, their structure, stability and formation, see the review by Eccleston [2] and the references therein. For additional details on the making of shampoos and conditioners, consult 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

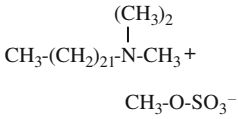
Creme rinses and most hair conditioners are basically compositions containing cationic surfactant in combination with long-chain fatty alcohol or other lipid components. Distearyldimonium chloride, cetrimonium chloride, stearalkonium chloride and behentrimonium methosulfate are typical cationic surfactants 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

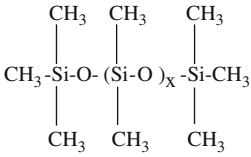


Cetrimonium Chloride



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:

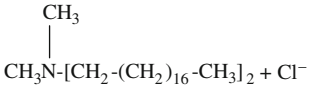
1. Lipid soils are the primary hair soil and are largely, but not entirely sebaceous matter. For a more complete description of the chemical composition of sebaceous soil, see Chap. 2.

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.

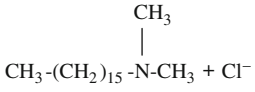
6.3.2 Soils from Hair Products

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) $£_{fw}$,

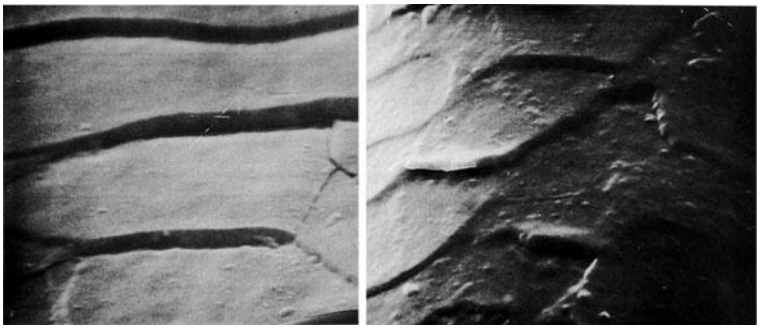


Fig. 6.2 Scanning electron micrographs hair fiber surfaces illustrating sebaceous soil (*Right*) versus a fiber cleaned with sodium lauryl sulfate solution (*Left*)

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.

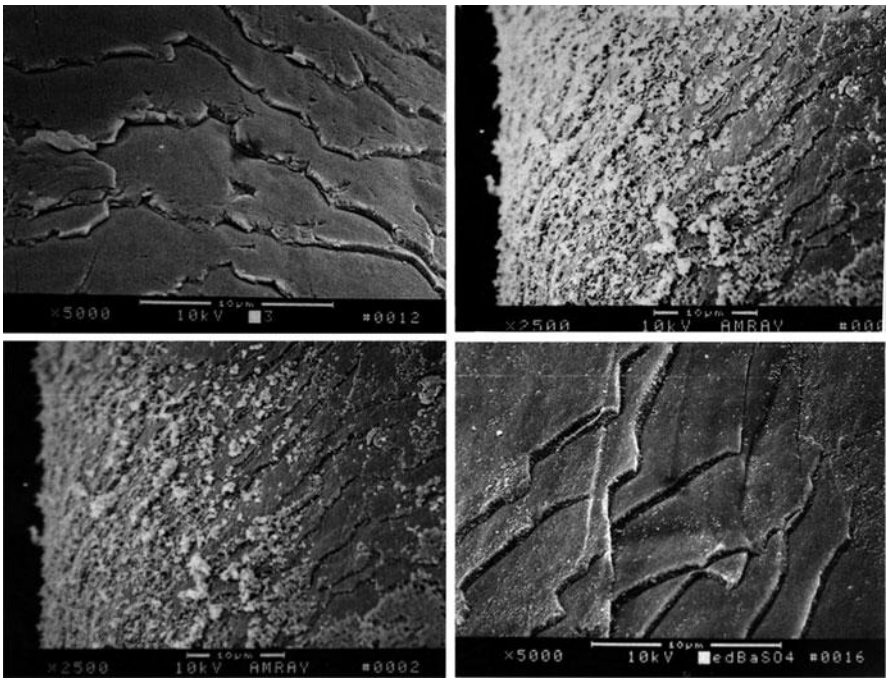


Fig. 6.3 Particulates on the surface of hair fibers. *Upper left*: control fiber with clean surface. *Upper right*: Barium sulfate particles on the surface. *Lower left*: Black iron oxide particles on the surface. *Lower right*: Precipitated fine Barium Sulfate on the hair surface

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.

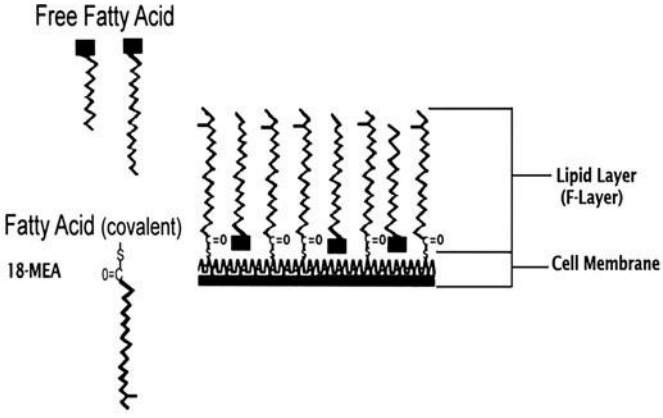


Fig. 6.4 Schematic illustrating the hair fiber surface with 18-MEA and free lipid on the external layer with epicuticle proteins on the second and third layers

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

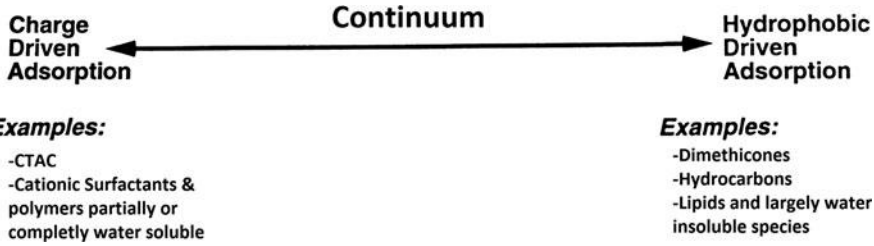


Fig. 6.5 Schematic illustrating the hypothesis [67] of a continuum between a charge driven and a hydrophobically driven mechanism for adsorption of conditioning agents to keratin surfaces

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

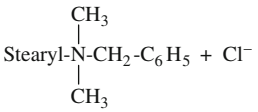
nature of the adsorbing ingredients. This property is determined by the ratio of nonpolar to polar substituent groups. If we are considering absorption, then we must consider diffusion rates that are governed primarily by molecular size, condition of the hair, pH and reaction temperature.

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.

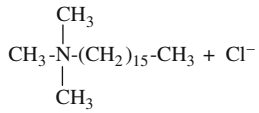
More anionic surfactant does bind to hair with decreasing pH, suggesting that low-pH shampoo formulations (below the isoelectric point) will leave more anionic surfactant behind after shampooing than neutral pH shampoos.

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

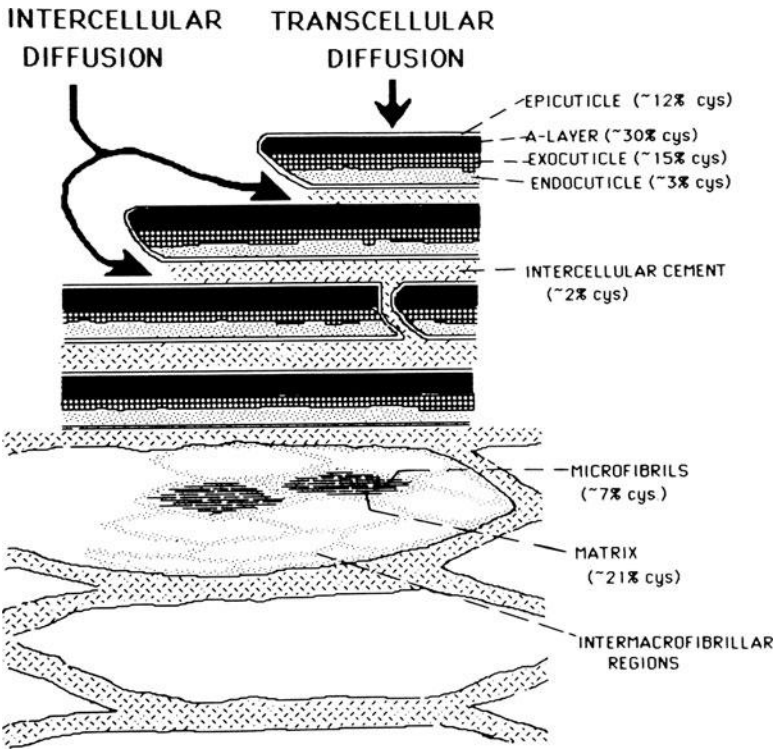


Fig. 6.6 Schematic illustrating transcellular versus intercellular diffusion. Note: the different histological regions are not drawn to scale

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

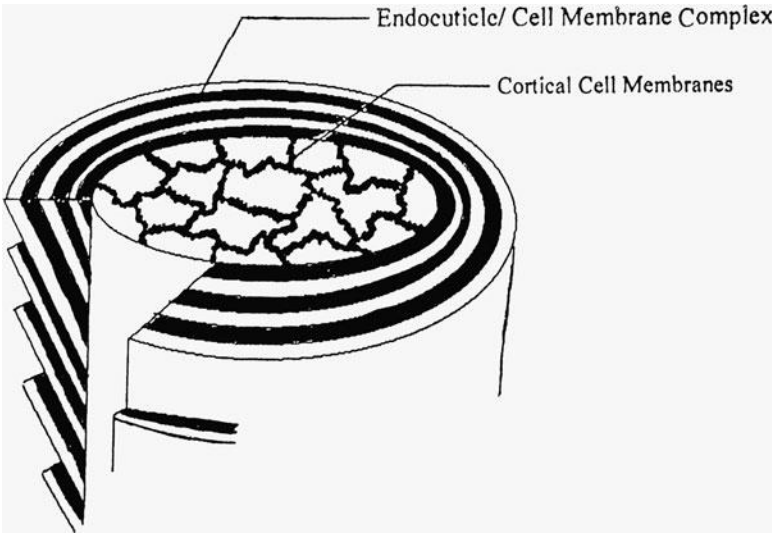


Fig. 6.7 Schematic illustrating the non-keratinous route for diffusion into hair

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.

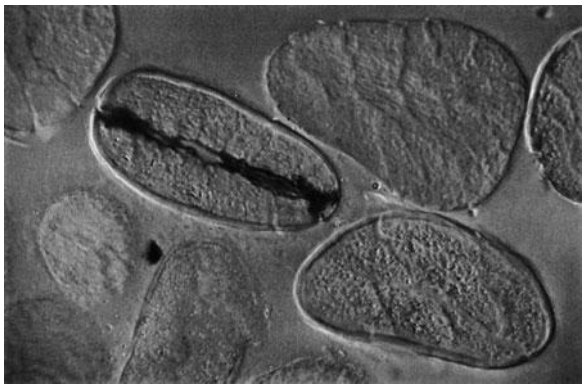


Fig. 6.8 Penetration of a cationic surfactant into a split hair. The split hair was treated with conditioner cross-sectioned and then stained with red 80 dye

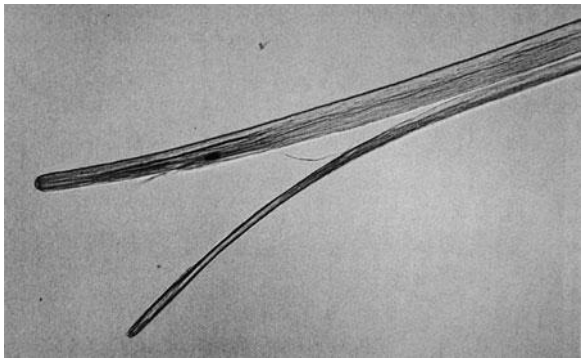


Fig. 6.9 Light micrograph of a split hair stained with red 80 dye after shampooing with sodium lauryl sulfate. Dye does not stain the hair with anionic adsorbed

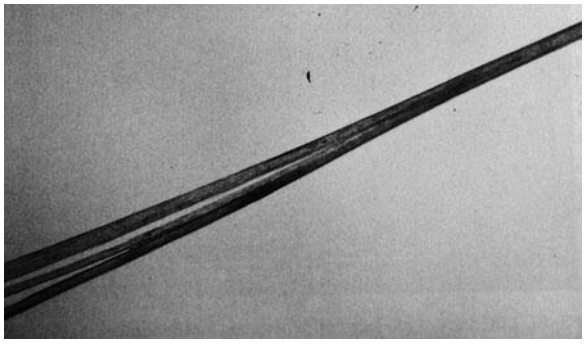


Fig. 6.10 Light micrograph of a split hair treated with a cationic conditioner and then stained with red 80 dye. Note staining on all surfaces including the split surface (where the cationic conditioner adsorbs). Compare to Fig. 6.9

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,

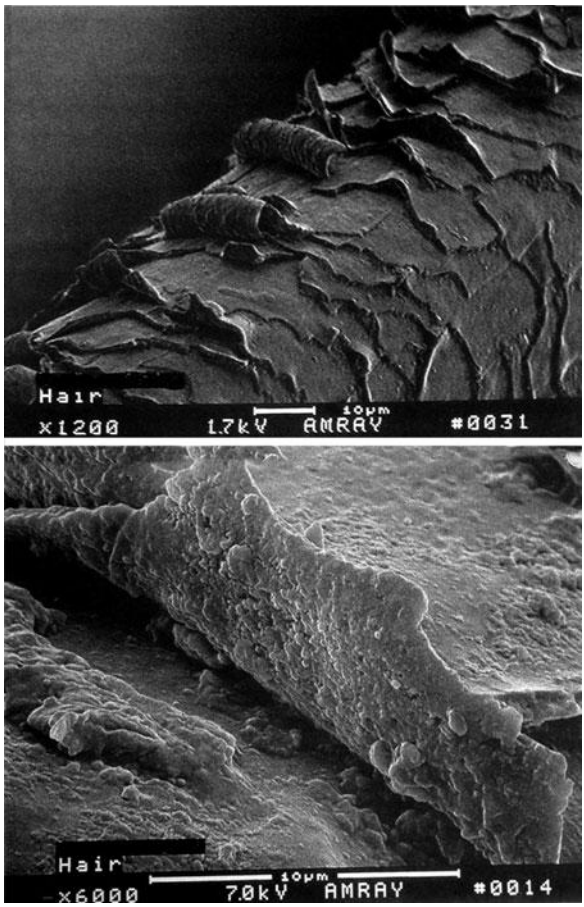


Fig. 6.11 Lifted scales from penetration and deposition underneath the scales. The treatment was alternating treatments of specific conditioner and shampoo ingredients

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,

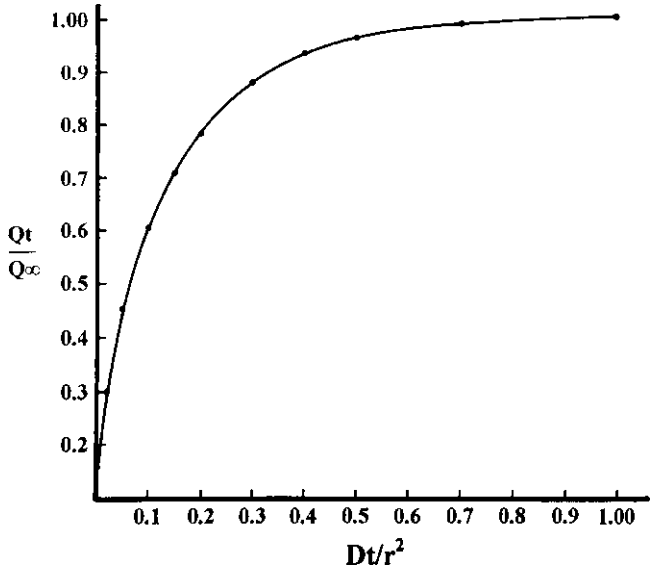


Fig. 6.12 Diffusion into a cylinder from an infinite bath. A plot from data by Vickerstaff. For lower proportions of penetration (See the data and plots by Vickerstaff [99])

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

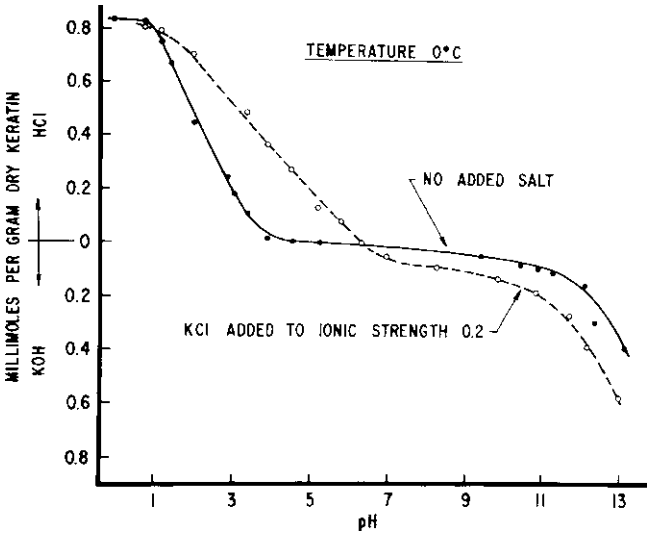


Fig. 6.13 The influence of salt on the combination of simple acids and base with keratin fibers (From data by Steinhardt, Fugitt and Harris [122])

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.

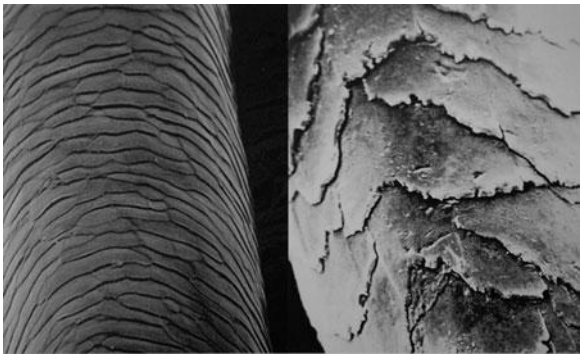


Fig. 6.14 SEMs illustrating damage from the chipping of scale edges. *Left*: SEM shows the fiber surface close to the scalp; note the smooth scale edges and faces. *Right*: SEM illustrates the fiber surface of about 1 year's growth and wear. Note the rough chipped and worn scales

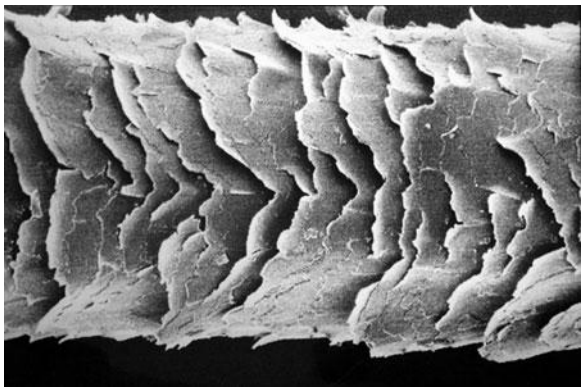


Fig. 6.15 Lifted scales from stretching at low RH (SEM provided by the courtesy of Sigrid Ruetsch)

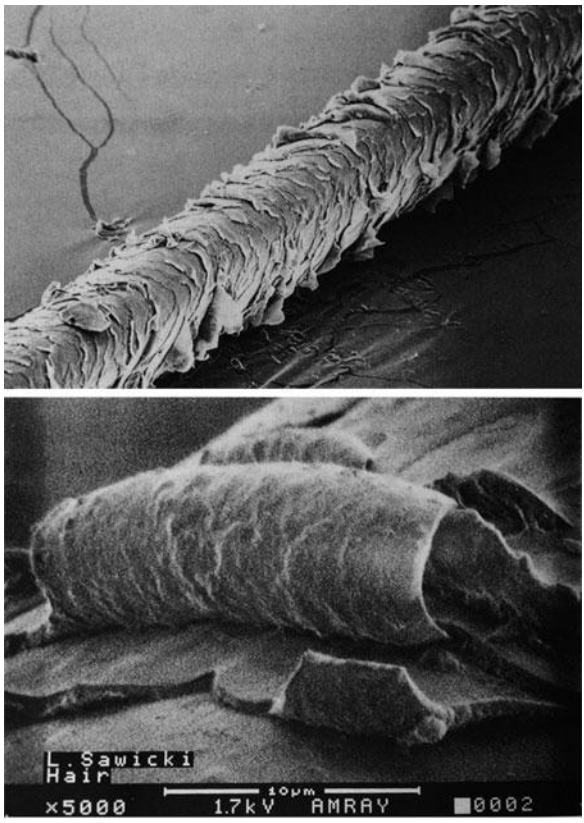


Fig. 6.16 Lifting of scales on permed-dyed hair by alternating treatments with TEA lauryl sulfate and stearalkonium chloride

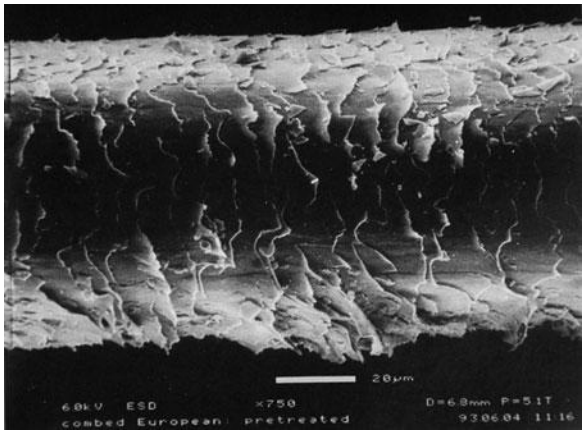


Fig. 6.17 Scale lifting caused by vigorous combing of hair tresses

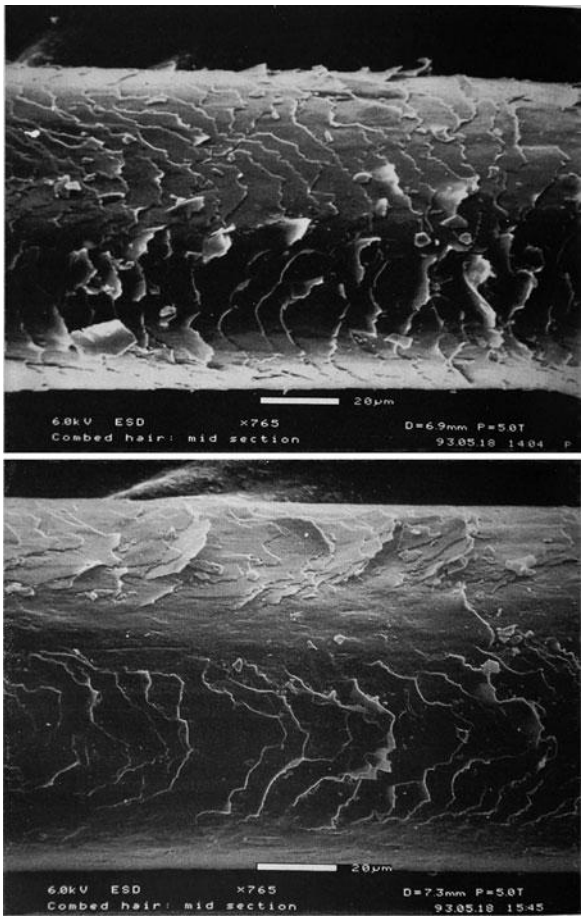


Fig. 6.18 Chipping, scale lifting and tearing of large sections of cuticle by vigorous combing

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

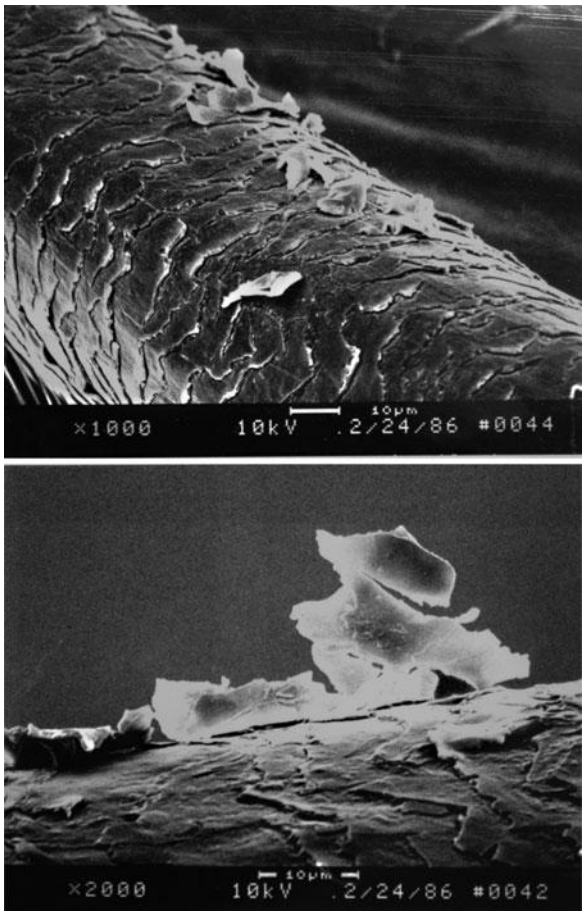


Fig. 6.19 Tearing or breaking off of large sections of a single cuticle scale after scale lifting

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.

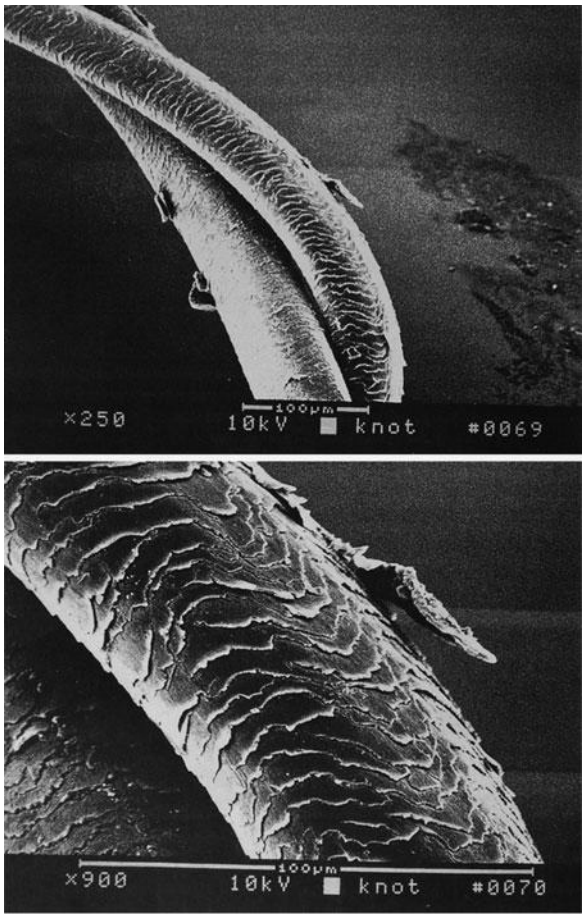


Fig. 6.20 Tearing of large sections of cuticle from hair on hair rubbing during knot formation

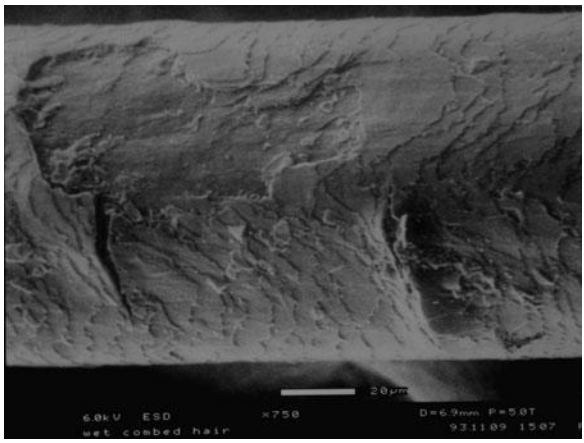


Fig. 6.21 Tearing of large sections of cuticle by vigorous combing of wet hair while heat drying

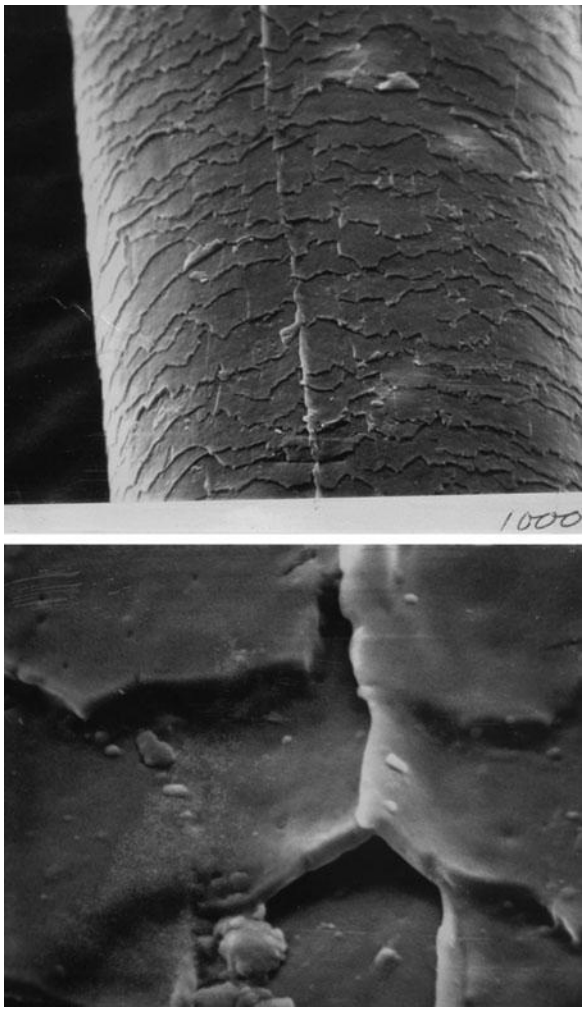


Fig. 6.22 Cuticle wear caused by sliding one single hair fiber (20 cm long) loop (wt. 0.58 mg) over two parallel fibers in a sliding friction experiment. See Chap. 9

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]

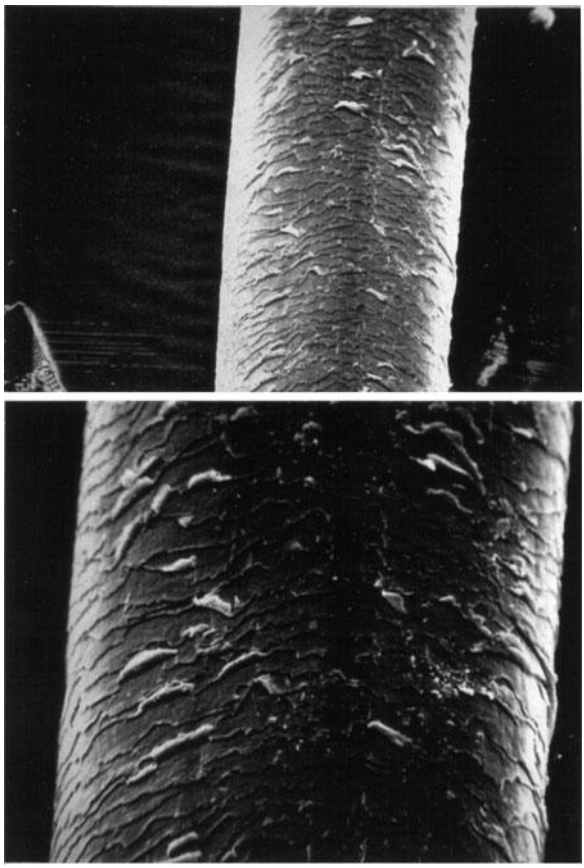


Fig. 6.23 Cuticle wear from a fiber from the experiment described under Fig. 6.22. Note the lines of wear and the folded back scale edges. This latter effect is from tip to root rubbing

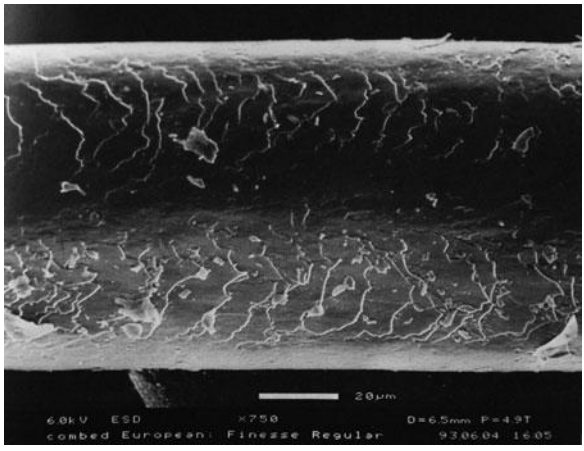


Fig. 6.24 Axial wear along a hair fiber from tress combing. This wear pattern is similar in type to that caused by the fiber loop experiment, illustrated in Fig. 6.22 (Micrograph provided by the courtesy of Elizabeth Gretler)

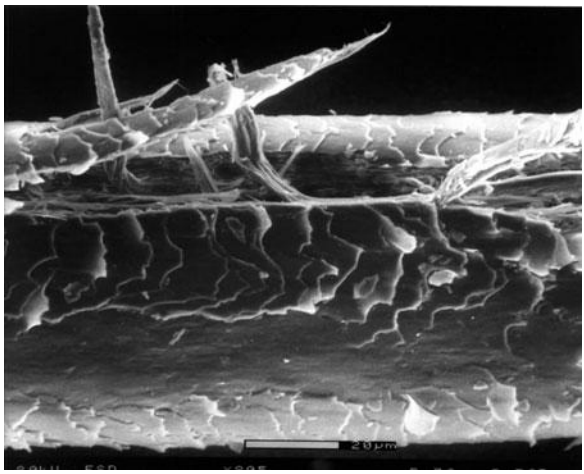


Fig. 6.25 Cortical lifting caused by back combing (teasing) of a tress (Micrograph provided by the courtesy of Elizabeth Gretler)

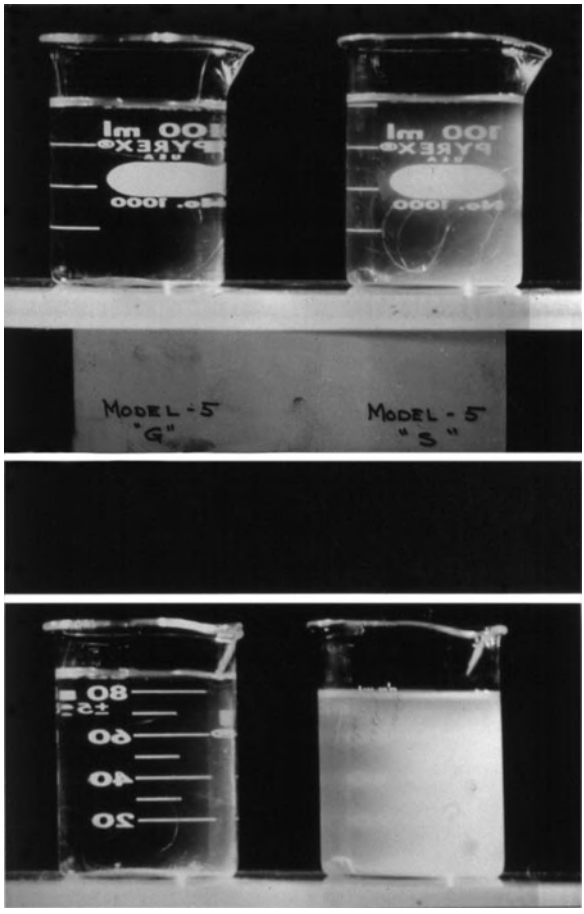


Fig. 6.26 Cuticle fragments collected from wet combing hair on heads and dipping the hair into water periodically (*G* is a conditioning shampoo and *S* is a cleaning shampoo)

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

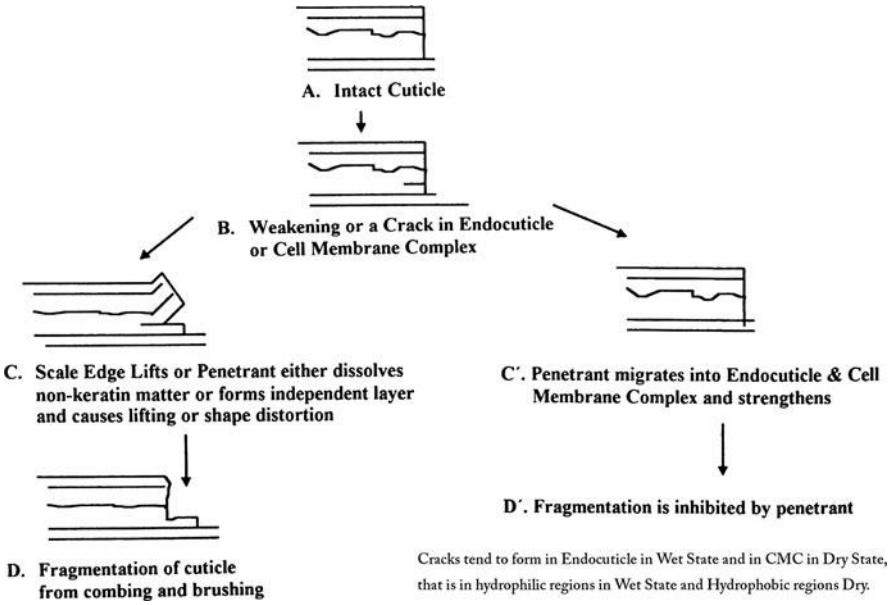


Fig. 6.27 Schematic diagram illustrating the process of cuticle fragmentation

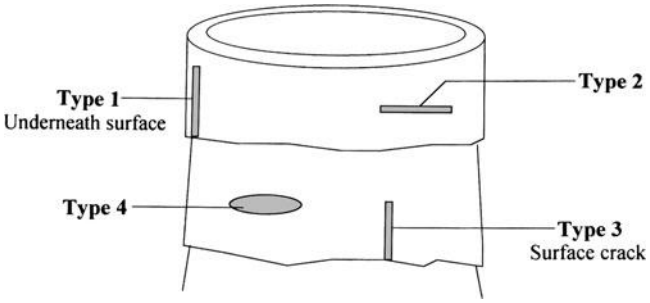


Fig. 6.28 Different types of cuticle cracks shown to form in human hair fibers

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

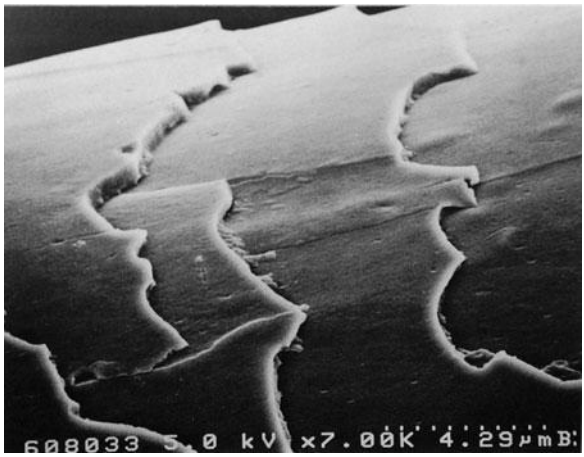


Fig. 6.29 Lightly damaged control hair surface. No cuticle cracks or lifting (SEM kindly provided by Sigrid Ruetsch)

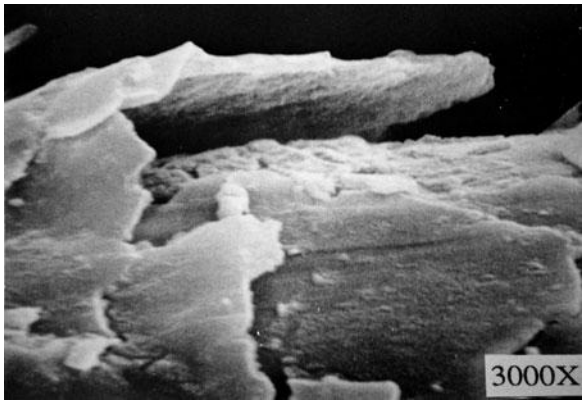


Fig. 6.30 Crack in the endocuticle formed from extending untreated hair (Type 1 crack) (SEM kindly provided by Sigrid Ruetsch)

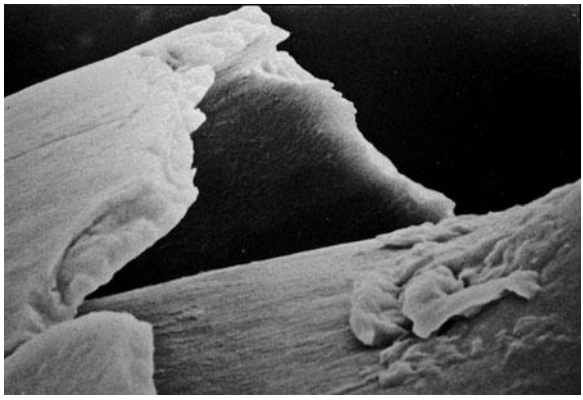


Fig. 6.31 Crack in the cell membrane complex formed by extending hair fibers wet. Note the smooth surfaces of the crack versus the rough surfaces of the endocuticular crack in Fig. 6.30 (SEM kindly provided by Sigrid Ruetsch)

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

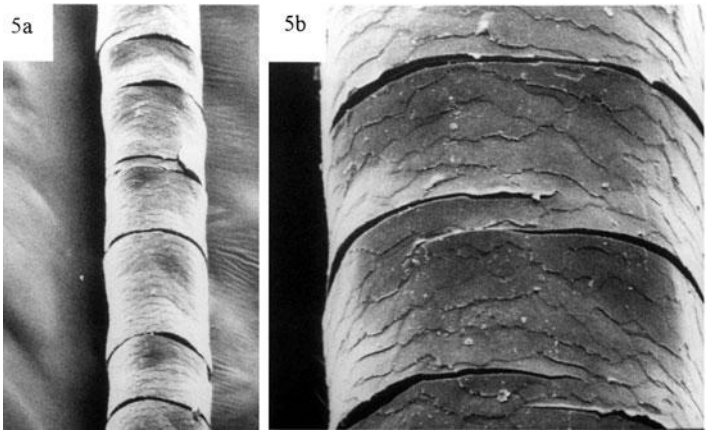


Fig. 6.32 Severe transverse cuticle cracks (Type 2) from extension cycling by Gamez-Garcia [160] (Reprinted with permission of the Journal of the Society of Cosmetic Chemists)

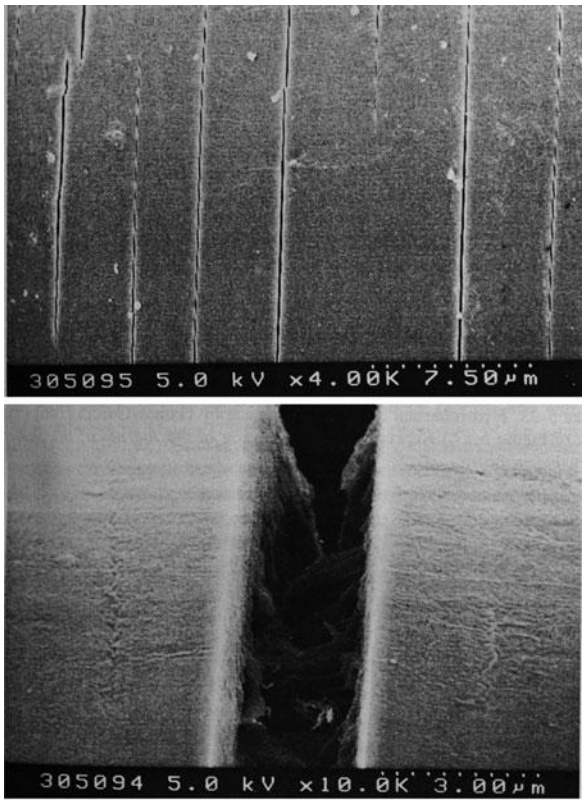


Fig. 6.33 Transverse cracks in the cuticle (Type 2 crack) from long term uv-exposure at high RH and extension (SEM kindly provided by Sigrid Ruetsch of Textile Research Institute)

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

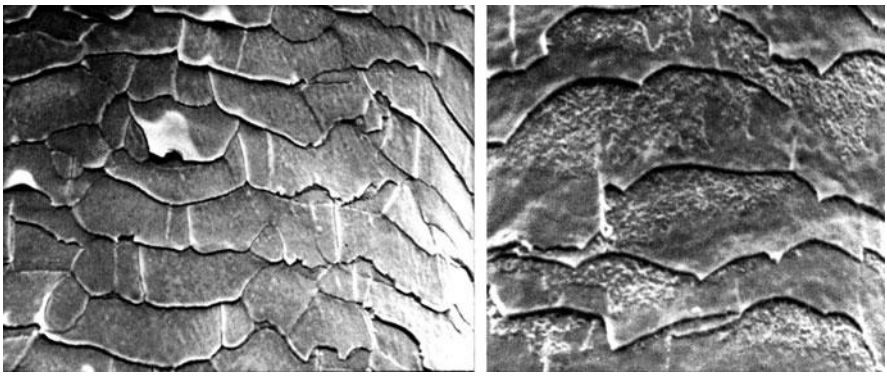


Fig. 6.34 Hydrothermal cracks in the cuticle from heat drying by Gamez-Garcia [161] (Type 3). *Left*: These cracks were produced by heat drying. *Right*: The same heat dried tress was combed producing this type of damage (Reprinted with permission of the Journal of the Society of Cosmetic Chemists)

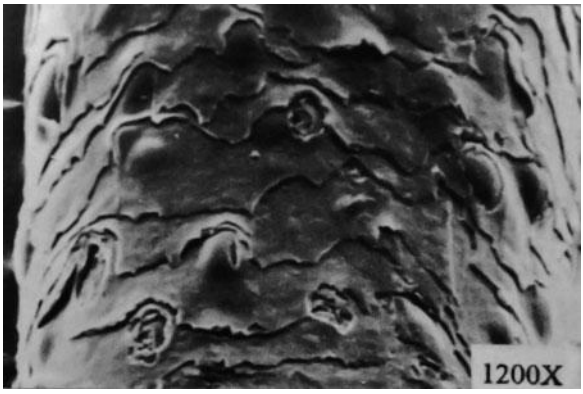


Fig. 6.35 Deep ovoidal cuticle cracks produced by thermal and extension cycling treatments by Garcia [149] (Reprinted with permission of the Journal of Cosmetic Science)

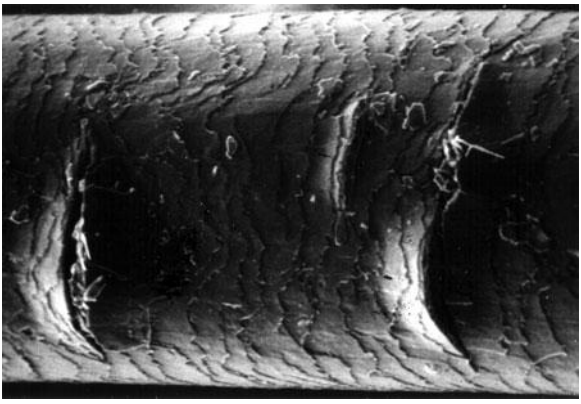


Fig. 6.36 Deep ovoidal cuticle cracks produced by vigorous wet combing and heat drying of hair

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.

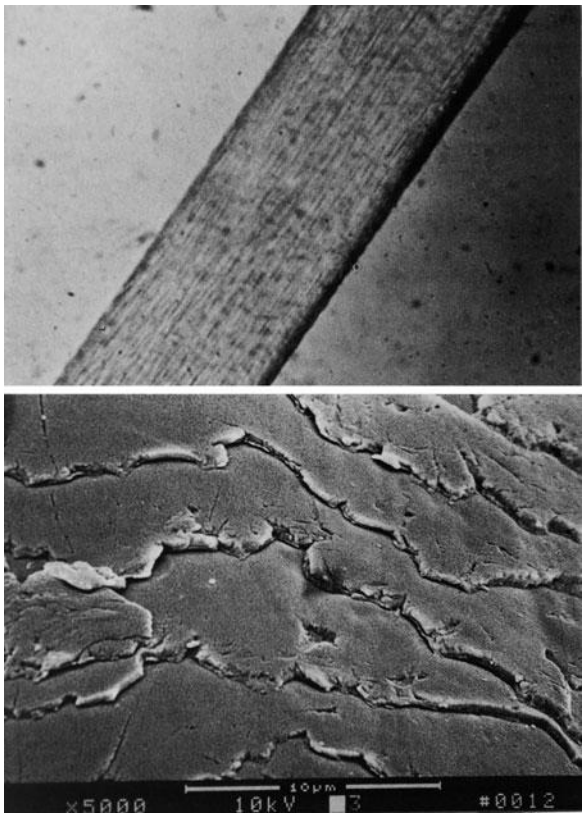


Fig. 6.37 Control fibers for penetration/deposition experiments. *Top*: Light micrograph in the wet state. *Bottom*: SEM illustrating the dry fiber surface

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

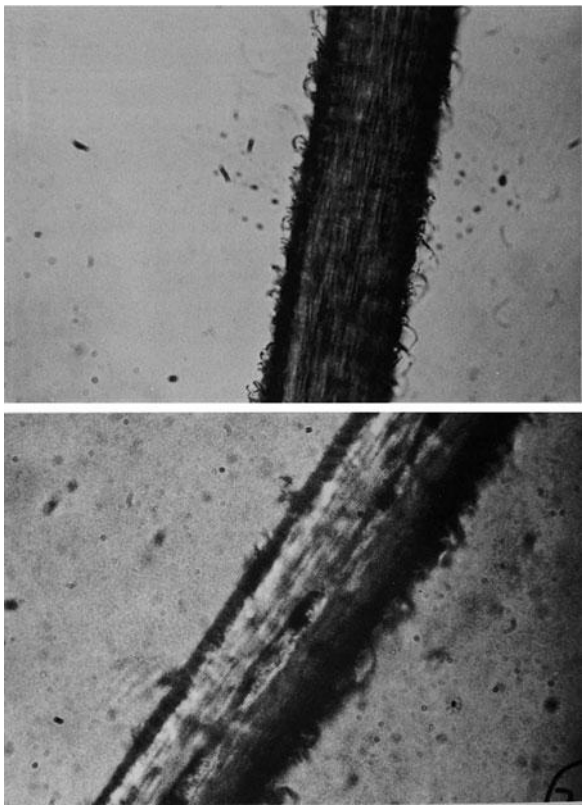


Fig. 6.38 Scale-lifting (in the wet state) by alternating treatments of TEA lauryl sulfate and stearalkonium chloride. Hair previously permed on a live head and subsequently treated in the laboratory

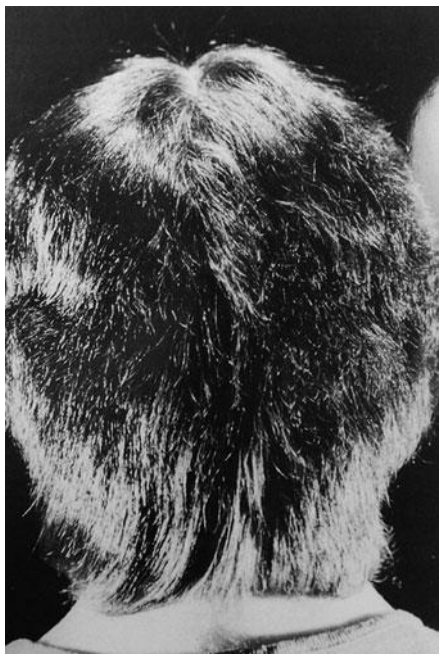


Fig. 6.39 Half head experiment. The *right side* was treated with alternating treatments of TEA lauryl sulfate and stearalkonium chloride. The *left side* was treated with sodium deceth-3 sulfate and stearalkonium chloride. Note the shine on the left side and the dullness on the right. This hair was originally permed and oxidatively dyed on the head of a panelist and worn for several weeks before the main treatment

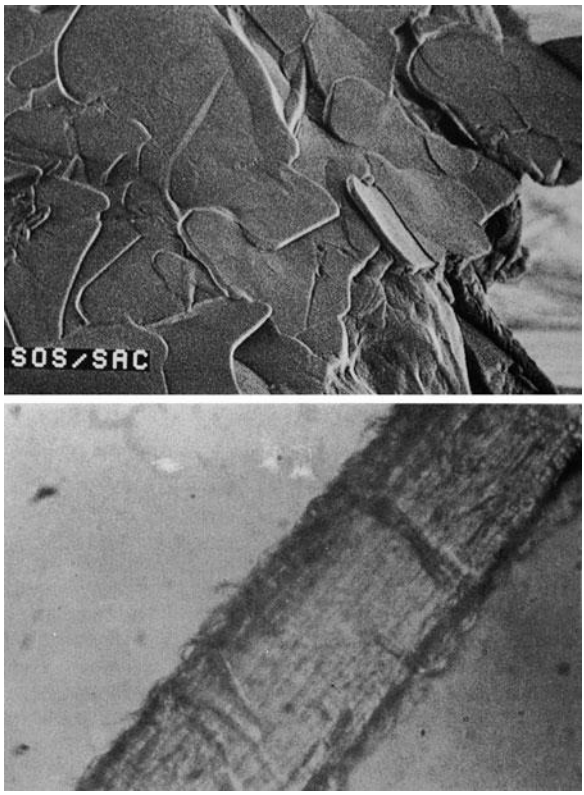


Fig. 6.40 Hair fibers treated in the laboratory with alternating treatments of sodium octyl sulfate and stearalkonium chloride. *Top*: SEM illustrating dry state effects. Note the scale damage and the large deposits. *Bottom*: Light micrograph illustrating the appearance of the fiber wet. Compare to 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

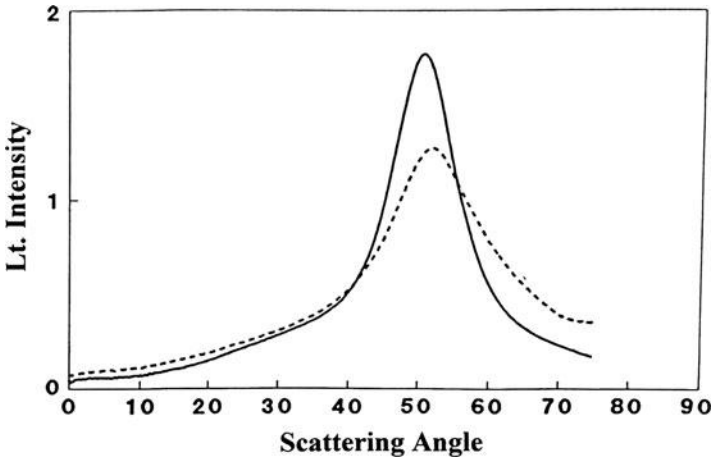


Fig. 6.41 Schematic of light scattering curves illustrating a normal untreated hair fiber (*solid line*) and a fiber with scales lifted (*dashed line*)

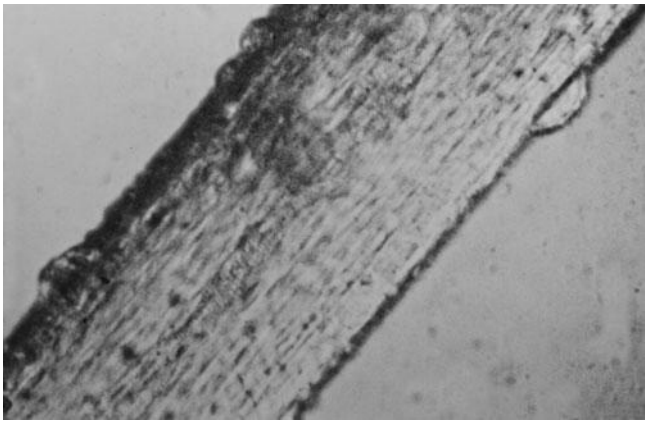


Fig. 6.42 Light micrograph of hair in water illustrating scale lifting caused by alternating treatments of a cleaning shampoo and a leading US hairspray

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.

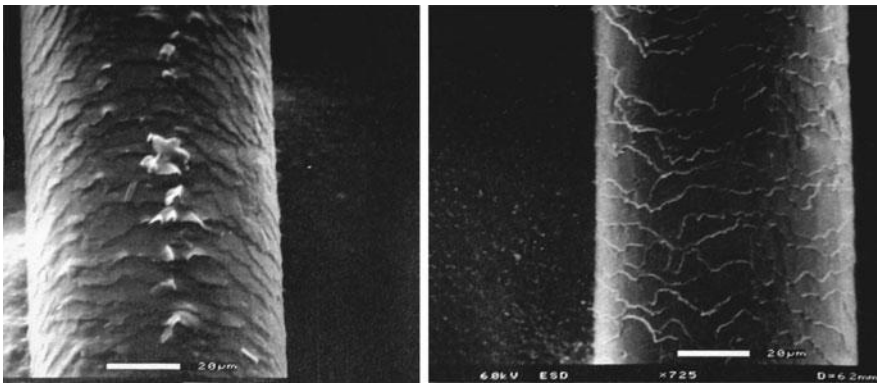


Fig. 6.43 Scale lifting by a leading US 2 in 1 shampoo. *Right*: Control treatment by a 2 in 1 shampoo that does not cause scale lifting. *Left*: The US 2 in 1 shampoo that caused scale lifting. This formula is no longer being sold

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)

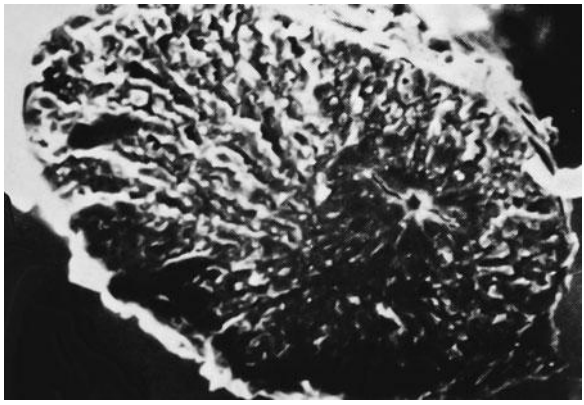


Fig. 6.45 Smooth fracture. Note the origin of the crack is close to the center of the fiber (SEM kindly provided by Sigrid Ruetsch)

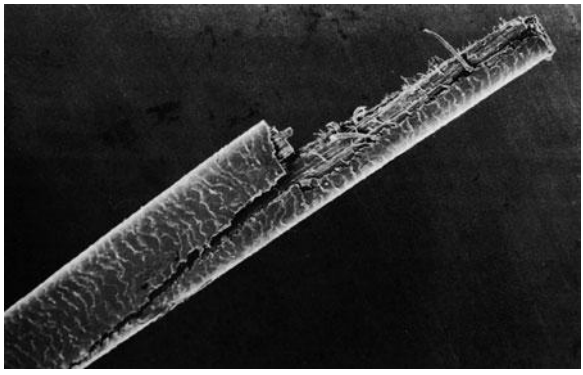


Fig. 6.46 Step fracture. Note the extension of the crack along the fiber length inside the step (SEM kindly provided by Sigrid Ruetsch)

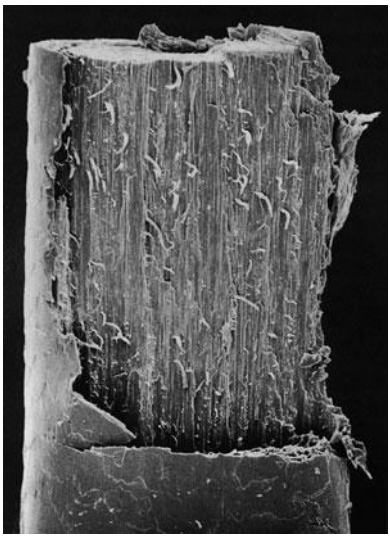


Fig. 6.47 Step fracture (SEM kindly provided by Sigrid Ruetsch)

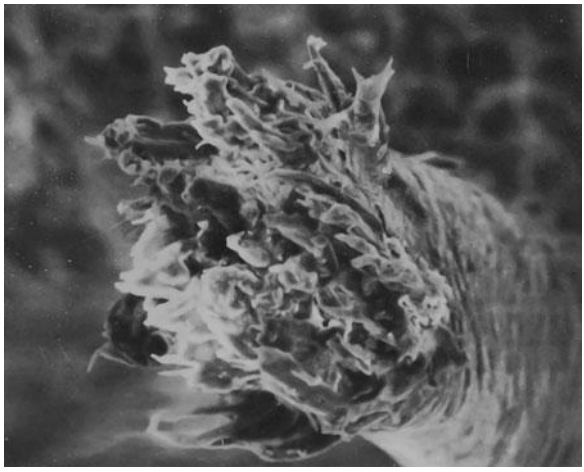


Fig. 6.48 Fibrillated end. Fiber fractured at 65% RJ [166] (Reprinted with permission of the Journal of the Society of Cosmetic Chemists)

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

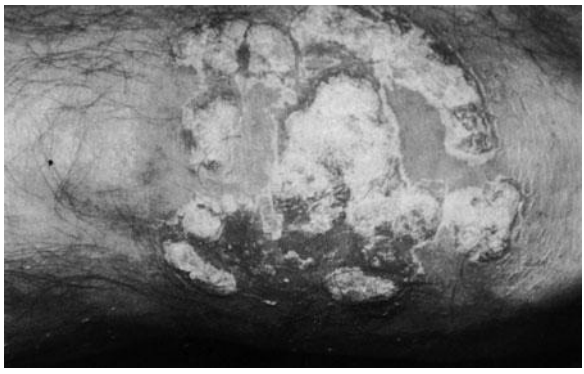


Fig. 6.49 Photograph illustrating the silvery scaly condition of psoriasis

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

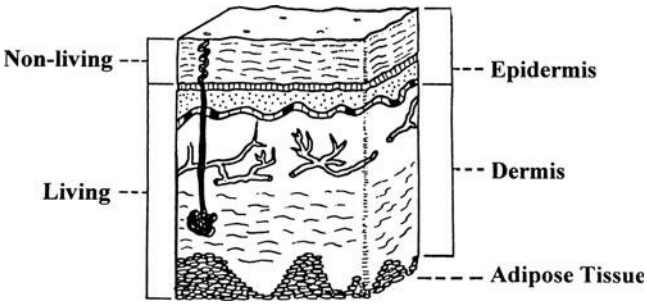


Fig. 6.51 Schematic diagram illustrating a section of human skin. Note the non-living barrier membrane called the stratum corneum

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,

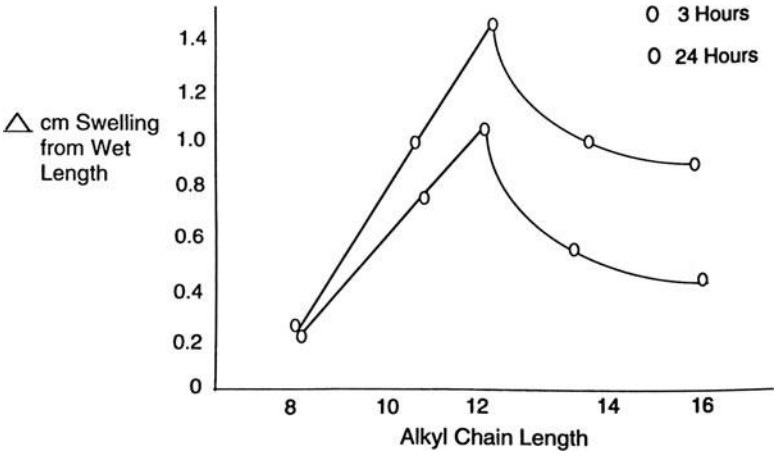


Fig. 6.52 Chain length of alkyl sulfates and skin swelling. Note the peak in swelling at an alkyl chain length of 12 carbon atoms [110] (Reprinted with permission of the Journal of the Society of Cosmetic Chemists)

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.

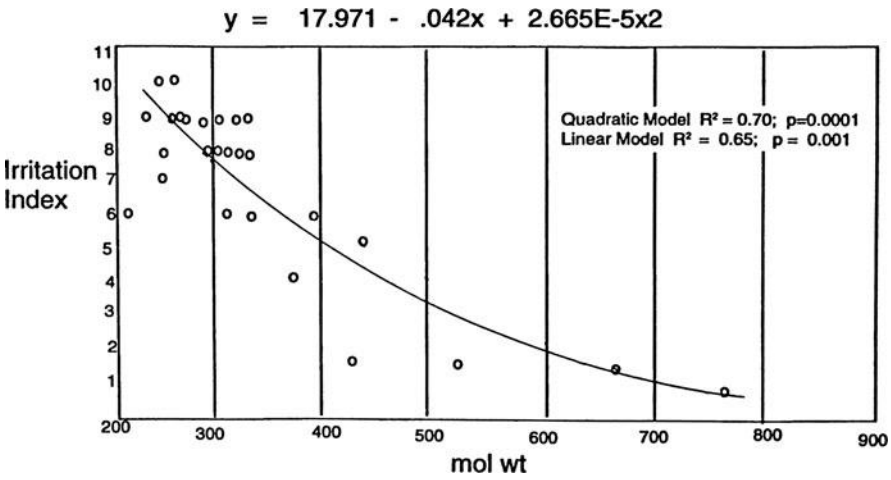


Fig. 6.53 Skin irritation and molecular weight of anionic surfactants. Note the decrease in irritation with increasing molecular weight (size)

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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