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Shampoos and Conditioners

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I. INTRODUCTION

The primary function of shampoos is to clean the hair, thereby improving its appearance through the removal of dulling deposits that can weigh the hair down and even cause it to stick together. The main function of conditioners is to reduce the magnitude of the forces associated with combing or brushing hair. This latter benefit is also provided, to differing extents, by conditioning shampoos, while both products can provide important secondary benefits such as dandruff control, hair moisturization, flyaway reduction, and improvement of shine.

In formulating shampoos and conditioners to provide the above benefits, several unique factors must be considered. The products must act quickly, of the order of minutes, and at relatively low temperatures between 20 and 40°C. The viscosity of the formulations must also be sufficiently high to avoid runoff from the hand while still spreading easily on the hair. In addition, a shampoo must generate a rich and stable lather that can be rinsed easily. Finally, since shampoos and conditioners will be used in contact with skin and eyes, they must exhibit low toxicity and irritation.

In this chapter the effects of these and other factors on product form and development are discussed. The first section describes general shampoo and hair conditioner compositions. Subsequent sections then discuss hair-cleaning mechanisms and product performance and efficacy, followed by methods of evaluating the cosmetic attributes of shampoos and conditioners. Finally, a brief discussion of damage to hair from shampooing and grooming is presented.

II. TYPICAL COMPOSITION AND INGREDIENTS

The basic ingredient composition of shampoos is summarized in [Table 10.1](#). Some additional ingredients are listed in [Table 10.2](#).

TABLE 10.1 Basic Ingredient Composition for Cleansing Shampoos

Basic ingredient	Activity (%)
Primary surfactants — anionic (e.g., ALES, ALS, AOS)	8–20
Secondary surfactants/foam boosters — nonionic and amphoteric (e.g., betaine, amine oxide, amphotacetate, sultaine, sulfosuccinate, APG)	0–10
Foam stabilizers (e.g., CDEA, CMEA)	0–5
Thickeners (e.g., salt, gum, polymer)	0–5
Other minors (preservatives, fragrance, acid, dye)	QS
Water	Balance

TABLE 10.2 Additional Ingredients for Various Shampoos

Additional ingredient	Activity (%)
Conditioning agents (e.g., silicones, cationic polymers, cationic surfactants, oils)	0–8
Pearlizing agents (e.g., EGDS, EGMS)	0.2–2.5
Opacifiers (e.g., cetyl stearyl alcohol)	0–3
Rheology modifiers (e.g., gum, polymer)	0–3
Emulsifiers	0–5
Clarifying agents	0–3
Antioxidants	0–2
Antidandruff/antifungal agents	0.5–5
Promotional additives (UV absorbers, natural oils, botanic extracts, protein hydrolytes)	0–2

A. Surfactants in Shampoos

To provide adequate cleaning, lather, and viscosity, shampoos generally contain surfactants at concentrations between 8 and 20%, along with fragrances, color additives, and preservatives. Other possible ingredients include conditioning agents, opacifiers, clarifying agents for solubilization, thickeners for viscosity control, and antidandruff agents. Many shampoos also contain special ingredients such as vitamins, pro-vitamins, antioxidants, and herbal and marine extracts. These special additives are employed to support innovative claims involving repair, revitalization, nourishment, and color protection of hair.

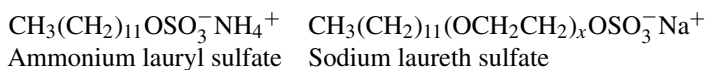
The surfactants in shampoos can be classified according to whether or not they carry a charge. With the exception of baby shampoos, most primary surfactants are anionic; other surfactants are generally used in a secondary capacity.

1. Primary Surfactants

The main function of the primary surfactants in a shampoo is to provide a cleaning benefit. Primary surfactants are also necessary for adequate foam and viscosity control. As stated above, levels of surfactant between 8 and 20% are generally employed in shampoos. These levels are chosen primarily to provide acceptable lather and viscosity, since many common soils, e.g., sebum, are adequately cleaned at lower surfactant concentrations.

(a) *Alkyl and Alkyl Ether Sulfates.* The most common primary surfactants used today in shampoos are the lauryl and lauryl ether (laureth) sulfates. These materials were first introduced into the U.S. market more than 50 years ago [1], and since then the lauryl (sodium or ammonium, triethanolamine, diethanolamine) and laureth (sodium or ammonium) sulfates have dominated the market, in large part because their properties represent an excellent balance of cost, mildness, cleaning efficacy, lather, and viscosity control.

The lauryl and laureth sulfates are used either alone or in combination. The most commonly used variants are ammonium lauryl sulfate (ALS) and sodium or ammonium laureth sulfates (SLES or ALES) with an average of 2 or 3 moles of ethylene oxide [2,3]:



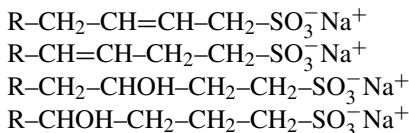
The lauryl sulfates are produced by sulfation of a mixture of synthetically prepared C₁₂–C₁₄ fatty alcohols or a mixture of coconut fatty alcohols (approximately 50% C₁₂). Depending on the manufacturer, the commercial lauryl and laureth sulfates contain different mixes of mostly C₁₂ and C₁₄ surfactants. These are chosen to improve the foam and surface activity of the species.

Schwuger [4] has investigated the effects of ether groups on the solubility, surface properties, and detergency of alkyl ether sulfates. Addition of ethylene oxide groups to the alkyl surfactants increases solubility, thus reducing the formation of precipitates and maintaining foam volume in the presence of Ca²⁺ and Mg²⁺ ions. The use of ether sulfates would be preferred over that of alkyl sulfates for a clear formulation.

The sulfate group is attached to the lauryl and laureth surfactants through an ester linkage. These detergents are therefore subject to hydrolysis at extreme values of pH. As a result, shampoos containing these surfactants are generally formulated with a pH between 5 and 9.

Minimal irritation is another essential property for shampoos because the products can easily come into contact with sensitive parts of the body, including the eyes, during the hair washing process. Studies on skin irritation by surfactants show that irritation is usually not a problem with the long-chain alkyl sulfates [5–9]. The presence of ethylene oxide groups reduces the irritation of these materials.

(b) *Alpha Olefin Sulfonates.* The alpha olefin sulfonates (AOS) rank second in use behind alkyl and alkyl ether sulfates. Nevertheless, because of the predominance of the latter surfactants, AOS has been confined to limited use in nonpremium shampoos. The detergent is actually a mix of four species in roughly equal quantities that can be represented by the following structures:



Commercial AOS is 14 to 16 carbons in chain length, so that R in the above structures represents a hydrocarbon chain length of 10 or 12.

AOS is fairly stable at low pH because the SO_3 attachment does not involve an ester linkage. It is therefore suitable for use in low pH formulations. It is also more soluble in hard water than SLS. Foaming of AOS has been reported to be comparable to SLS and SLES under various conditions especially in the presence of sebum [10,11]. Other distinctive properties that AOS exhibits include low cloud point, good solubilizing properties, and light color and odor.

Viscosity building with AOS is more difficult than with alkyl sulfates, although it can be done with the same types of materials, such as monoalkanolamides and salt [11–13]. In addition, the detergent has been reported to leave a harsher feel than lauryl and laureth sulfates [13].

2. Secondary Surfactants

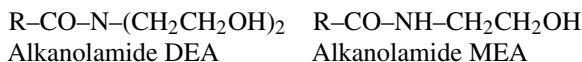
Secondary surfactants, which include nonionics, amphoterics, and some of the less widely used anionics, are often employed in a formulation to improve foam quality and stability, to provide additional detergency, and to enhance viscosity. Some of them are also used to reduce eye irritation in mild or baby shampoos.

(a) *Nonionic Surfactants.* Although the detergency of nonionic surfactants is equal to, or in many cases better than, that of anionic surfactants [14,15], nonionic detergents have not been used as primary hair cleansers due to their inferior foaming properties. This is because of the large surface area per molecule and the lack of charge on the surface films of nonionic foam [16].

An example of a nonionic for baby shampoos is Polysorbate 20, which is the monoester of lauric acid and anhydrosorbitol condensed with approximately 20 moles of ethylene oxide. Another example is PEG-80 sorbitan laurate, an ethoxylated sorbitan monoester of lauric acid with an average of 80 moles of ethylene oxide.

Fatty alkanolamides are another class of commonly employed nonionic surfactants. These are used in shampoos to enhance lather and viscosity. The most frequently used alkanolamides are cocoamide DEA (diethanolamide) and

cocoamide MEA (monoethanolamide):

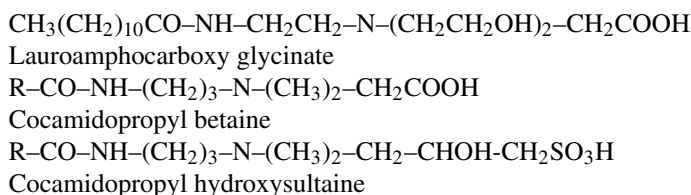


where R is a hydrocarbon chain that, in the case of lauramide, for example, would contain 11 carbons. The monoethanolamides are reported to enhance viscosity more effectively than the corresponding diethanolamides [17,18].

The viscosity-building effect of the long-chain amides is a result of the building of ordered structures between detergent and amide molecules. This effect is promoted by the linear alkyl chain in the surfactant, which lines up easily to form ordered arrangements [1,3].

Amine oxides are also employed to improve foam characteristics and stabilize lather, especially at moderately acidic pH values. CAP (cocamidopropyl) amine oxide is one of the most commonly used amine oxides. These materials act as nonionics at the near-neutral pH encountered in shampoos but are easily protonated at acidic pH. As a result, they sometimes behave as cationics and act as conditioning and antistatic agents as well in a properly formulated system [13,19].

(b) *Amphoteric Surfactants.* Amphoteric surfactants are often used in conventional and baby shampoos to improve mildness and lather. Examples include lauroamphocarboxy glycinate [20], CAP betaine, and CAP hydroxysultaine:



Betaines are very soluble over a wide pH range. Their charge nature changes with pH. At high pH the surfactant is anionic as a result of ionization of the carboxyl group, while at low pH the nitrogen is protonated, resulting in a cationic species. At the intermediate pH values normally found in shampoos, the carboxyl group is partially ionized and the nitrogen is partially in the protonated form.

In general, betaines are compatible with anionic surfactants. The simpler alkyl betaines are found to be less compatible with alkyl sulfates than the alkylamido-propyl betaines, especially when the concentration of betaine is about one half that of the lauryl sulfate [1]. This incompatibility is related to the pH of the system as well as the nature of the anionic species present.

Betaines act as foam modifiers, changing the loose and lacy foams normally generated by lauryl and laureth sulfates to thick and creamy lathers. They also help to thicken shampoo formulations and lower eye and skin irritation [21,22].

(c) *Miscellaneous Anionic Surfactants.* There are many other anionic surfactants that have been used at low concentration as secondary surfactants in shampoos or other specialty products. The materials on the list include paraffin sulfonate, alkylbenzene sulfonate, sulfosuccinates, linear alkylbenzene sulfonates,

N-acyl methyltaurates, *N*-acyl sarcosinates, acyl isethionates, *N*-acyl polypeptide condensates, polyalkoxylated ether glycolates, monoglyceride sulfates, and fatty glyceryl ether sulfonates [1,23].

B. Conditioning Agents in Conditioners

Hair conditioners are used primarily to improve the appearance and manageability of hair. They can be either rinse-off or leave-in types having the form of emulsions, solutions, or creams, and having a wide range of viscosities. There is also a wide range of claimed benefits associated with different conditioners, such as improved ease of combing, reduction of damage from grooming, prevention of flyaway hair, and increased hair softness and shine.

Several major types of conditioning agents have been employed in conditioners including cationic quaternary ammonium compounds, cationic polymers, long-chain fatty alcohols, and silicones such as dimethicone and its derivatives. These conditioning agents provide various cosmetic benefits to hair and may exhibit different drawbacks. For example, some silicones may leave a greasy feel on dry hair. Use of high concentrations of cationic polymers, which bind strongly to the hair surface at multiple sites, may lead to over-conditioning and excessive buildup after repeated application. Therefore, combinations of different types of conditioning agents are often used to provide the best overall conditioning performance.

Most products, however, contain the same general classes of conditioning agents with differences mainly in concentrations, numbers of different agents, and the particular members of a conditioning class employed. Table 10.3 lists a formula example from U.S. Patent 6,287,545 for a rinse-off conditioner.

The major classes of conditioning agents are described in the following sections.

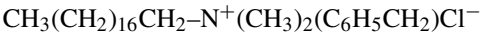
TABLE 10.3 Formula Example from U.S. Patent 6,287,545 for a Rinse-Off Conditioner

Ingredient	Activity (%)
Stearyl alcohol	1.00
Cetyl alcohol	3.00
Stearamidopropyl dimethylamine	1.00
Distearyldimonium chloride	0.75
Dimethicone	0.75
Mineral oil	0.55
Cyclomethicone	0.75
Propylene glycol	0.50
Fragrance and preservative	0.50
Water	QS to 100

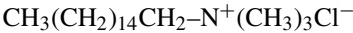
1. Cationic Surfactants

Cationic surfactants, primarily quaternary ammonium compounds (quats), are the most widely used conditioning agents in current commercial products [24–26]. Important reasons for this include effectiveness, availability, versatility, and low cost.

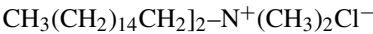
Examples of commonly used quats are stearalkonium chloride, cetrimonium chloride, and dicetyldimonium chloride:



Stearalkonium chloride



Cetrimonium chloride



Dicetyldimonium chloride

Because of the positive charges on quaternary ammonium compounds, such as the above, they are substantive to hair, binding to negative sites on the hair surface. Treatment with these materials, therefore, results in a hydrophobic coating on the hair fiber that not only renders the hair softer and easier to comb [27] but also greatly reduces the buildup of static charge (flyaway) on the hair surface [28].

Deposition of conditioning quats has been found to increase with increasing negative charge on the hair surface. Thus, deposition is greater on chemically treated hair (bleached, permed, or dyed), which is oxidized as part of the treatment process and therefore carries a greater negative charge. Deposition is also greater on the tips of the hair, which are older and therefore subject to greater sunlight oxidation. This can be seen in Table 10.4, which lists deposition from a solution of stearalkonium chloride on the roots and tips of bleached and virgin hair [29].

Many conditioning properties of quaternary ammonium compounds are related to the degree of hydrophobicity of the lipophilic portion of the surfactants. Thus quat deposition increases with increasing alkyl chain length and also with an

TABLE 10.4 Binding of Radiolabeled Stearalkonium Chloride (SAC) to Human Hair^a

Hair type	mg SAC bound/g hair (root area) ^b	mg SAC bound/g hair (tip area) ^b
Albino virgin hair	0.789	0.649
Albino bleached hair	1.62	1.83

^aTest procedure: 0.67 g of 1% [¹⁴C]SAC (30% ethanol:water) was applied to a 2 g tress and rubbed into the hair for 1 minute. Tresses were then rinsed in a beaker of tap water for 45 seconds, followed by rinsing in a second beaker for 15 seconds, and finally rinsed under running 38°C tap water for 1 minute. Portions of hair taken from different parts of the tress were then dissolved in 2M NaOH at 80°C, oxidized with H₂O₂, then mixed with Aquasol-2 LSC cocktail and perchloric acid and counted.

^bEach number represents an average of 5 replicates.

increase in the number of alkyl chains [30–35]. As a result, tricetylmonium chloride deposits to a greater extent than does dicetyldimonium chloride, which, in turn, is more substantive than the monocetyl quat.

Increased hydrophobicity has also been found to correlate with increased conditioning. Thus, Garcia and Diaz [36] have reported greater improvements in wet combing from heavier conditioning quats, even when present on hair in lower amounts than less hydrophobic species.

The dependence of deposition on degree of hydrophobicity indicates that van der Waals forces play an important role in deposition of quaternary ammonium conditioners [35]. This conclusion is consistent with the entropy-driven deposition demonstrated by Ohbu *et al.* [37] for a monoalkyl quat and by Stapleton [38] for a protonated long-chain amine.

2. Lipophilic Conditioners

In commercial products quaternary ammonium surfactants are almost never used alone. They are often used in combination with long-chain fatty conditioners, especially cetyl and stearyl alcohols [25], which serve to boost the conditioning effects of the quats [39]. The addition of cetyl alcohol to cetrimonium bromide was found to reduce combing forces by nearly 50% [25]. In another study, Fukuchi *et al.* [40] found a significant decrease in surface friction with the combination of cetyl alcohol and behentrimonium chloride.

Another consequence of the addition of fatty alcohols to cationic surfactants is the formation, under the right conditions, of liquid crystal and gel networks [41–45] that can greatly increase viscosity and confer stability upon the emulsion. Formation of such liquid crystals has been observed even at low concentrations [44,45]; the ready formation of these structures, along with low cost, improved stability, and compatibility with cosmetic ingredients are important reasons why long-chain alcohols are so ubiquitous in conditioning formulations.

Other lipids found in conditioners include glycol, triglycerides, fatty esters, waxes of triglycerides, and liquid paraffin.

3. Quaternized Polymers

Quaternized polymers have been found to improve wet combing and reduce static charge. In general, they can be formulated with anionic surfactants; greater deposition occurs with a mixture of amphoteric and nonionic surfactants. Two of the most important examples are Polyquaternium-10, a quaternized hydroxyethylcellulose polymer, and Polyquaternium-7, a copolymer of diallyldimethylammonium chloride and acrylamide. These are the two most frequently used polymeric conditioning agents in commercial shampoos [46,47].

Other important polymers are Polyquaternium-11, a copolymer of vinylpyrrolidone and dimethylaminoethyl methacrylate quaternized with dimethyl sulfate.

Also used are Polyquaternium-16, a copolymer of vinylpyrrolidone and quaternized vinylimidazole; and Polyquaternium-6, a homopolymer of diallyldimethylammonium chloride.

By virtue of their cationic nature, the above polymers are very substantive to hair. As a result of multiple points of electrostatic attachment to the hair fiber, they are also difficult to remove completely, especially when charge density is high [29,46]. It has been reported that deposition of many polymers on hair is inversely proportional to cationic charge density [48,49]. This was explained by the observation that smaller quantities of high-charge-density polymers would be needed to neutralize all of the negative charge on a hair fiber.

In a shampoo formula, Polyquaternium-10 and Polyquaternium-7 form negatively charged complexes with excess anionic surfactant [48,50]. These complexes are repulsed by the negatively charged hair surface, resulting in reduced deposition. The magnitude of this effect is determined by the particular anionic employed and the anionic surfactant/polymer ratio.

Despite the reduction in deposition, it has been reported that polyquaternium-SLS complexes resist removal from hair [51]. Therefore, care must be taken in formulating polyquats into both conditioners and conditioning shampoos to avoid excessive buildup and a heavy-coated feel on the hair with repeated use.

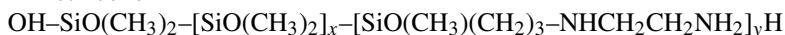
4. Silicones

The use of silicones in hair care products has increased considerably in the past two decades due to the pleasing aesthetic properties they impart to the hair. They are used in a wide variety of products, including conditioners, shampoos, hairsprays, mousses, and gels [52]. The low surface free energy of these materials results in rapid formation upon deposition of a thin, uniform coating on the surface of hair [53].

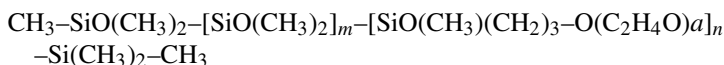
Silicones have been claimed to improve combing, enhance feel, reduce flyaway, increase shine, reduce drying time, and lock in color [54–56]. The most frequently used silicone is dimethicone, which is a polydimethylsiloxane. Other important silicones are dimethiconol, which is a dimethylsiloxane terminated with hydroxyl groups, amodimethicone, which is an amino-substituted silicone, dimethicone copolyol, which is a dimethylsiloxane containing polyoxyethylene and/or propylene side chains, and cyclomethicone, which refers to a class of cyclic dimethyl polysiloxanes ranging from trimer to hexamer:



Dimethicone



Amodimethicone



Dimethicone copolyol

The presence of amino groups in silicones was found by Wendel and Disapio [57] to greatly increase the substantivity of these materials. This is a result of the positive charge formed by these groups at the pH commonly found in commercial products.

In another experiment, Berthiaume *et al.* [53] found that deposition from a prototype conditioner formulation, as well as conditioning, softness, and detangling, increased with increasing amine content in a series of amodimethicones.

The relative conditioning efficacy of silicones and a series of cationic surfactants was compared [58]. It was found that dimethicone lowered frictional coefficients and surface energy of virgin hair to a greater extent than most cationic surfactants including a very effective conditioning agent, distearyldimemonium chloride. Dimethicones with molecular weight greater than 20,000 were found to be the most effective in reducing surface tension.

Synergistic effects have been observed when silicones are used in combination with a particular quat [59,60]. Deposition of silicones (30-second exposure followed by drying without rinsing) was found to nearly double if tricetyldimonium chloride was present in the silicone treatment solution. Reduction in combing forces was also almost doubled when silicones were deposited in the presence of the quat.

Dimethicone copolyols provide lighter conditioning effects due to their solubility in water and low level of substantivity. Because of that, they are less effective in rinse-off products. They are used, however, in leave-on products, such as hairsprays, styling mousses, and gels.

Cyclomethicone is volatile and does not remain on dry hair, especially after blow-drying. It helps other conditioning agent disperse, however, and form films on hair. It also helps improve wet combing and provides transient shine.

Silicones, especially dimethicone, have been employed as the primary conditioning agents in "two-in-one conditioning shampoos since the latter part of the 1980s. The level of conditioning from these types of shampoos is generally lower than that from stand-alone conditioners, especially on treated hair, which is more negatively charged and, therefore, has a lower affinity for hydrophobic substances like dimethicone.

Yahagi [58] studied the performance of dimethicone, amodimethicone, and dimethicone copolyols in two-in-one shampoos. Dimethicone and amodimethicone were found to provide hair with a similar degree of ease of combing. Unsurprisingly, soluble dimethicone copolyols did not perform well. Effects of silicones on foam volume were also investigated. A significant reduction in foam volume was observed with a model shampoo formula containing dimethicone, while amodimethicone and dimethicone copolyol showed a minimal effect on lather.

Table 10.5 lists various patents on hair conditioners granted since 1981. The development of more effective formulations with multiple benefits using novel

TABLE 10.5 U.S. Patents Related to Hair Conditioners and Conditioning Agents for Hair Care

Patent no. and year	Inventor(s) and company	Technology	Claimed benefits
U.S. 6730641 (2004)	Verboom <i>et al.</i> (Alberto-Culver)	Cetrimonium chloride/stearalkonium chloride = 0.65–2.0; $\leq 1\%$ total amount of cetrimonium chloride + stealkonium chloride	Synergistic effect; rinse-off or leave-in conditioner; provides silk wet feel and inhibits flyaway at 34% RH
U.S. 6726903 (2004)	Rutherford <i>et al.</i> (Unilever)	Monoalkyl quat ($\geq C_{14}$, C_{16} – C_{22})/dialkyl quat = 15:1–2:1; C_{16} – C_{16} dialkyl/ C_{18} – C_{18} dialkyl = 1:3–3:1	Foaming hair conditioner
U.S. 6723309 (2004)	Deane	Mixtures of conditioners, cooling agents, humectants, botanicals, and vitamins; No harsh chemicals and surfactants	Clean hair without removing essential oils; leave hair shiner, more body, and more manageable
U.S. 6645480 (2003)	Giles (Unilever)	Cationic surfactant; hydrophilically substituted cationic surfactant; lipid	An anionic surfactant-free formula providing acceptable cleaning and lathering; give wet slippery feel to hair
U.S. 6613316 (2003)	Sun <i>et al.</i> (Unilever)	Monoalkyl quat ($\geq C_{14}$, C_{16} – C_{22})/dialkyl quat = 15:1–2:1; monoalkyl quat ($\geq C_{14}$, C_{16} – C_{22})/dialkyl quat = 15:1–2:1; C_{16} – C_{16} dialkyl/ C_{18} – C_{18} dialkyl = 1:3–3:1; fatty alcohol opacifier	Opacifying hair conditioner
U.S. 6602494 (2003)	Jahedshoar <i>et al.</i> (Wella)	Silicone surfactant; hydrophobic, nonsurfactant silicone; basic or cationic N-containing conditioning compound; Polyhydric alcohol	Optically clear, transparent or translucent hair conditioner; leave-in or rinse-off

U.S. 6569414 (2003)	Bernecker <i>et al.</i> (Henkel)	Lipid-soluble ester alcohol or ester polyol; water-soluble compound (panthenol and derivatives, sugar, polyvinyl pyrrolidine or mixtures)	Reduce split ends
U.S. 6537533 (2003)	Alvarado (Unilever)	(a) C ₂₀ –C ₂₄ quaternary ammonium having ethosulfate or methosulfate as an anion; (b) C ₂₀ –C ₂₄ quaternary ammonium having chloride or bromide as an anion; (a)/(b) = 1:10–10:1; a solid at room temperature containing a fatty alcohol, ester, amine, amide, acid, or a water-soluble polymer	Nonirritating to eyes; rinse-out conditioner
U.S. 6376455 (2002)	Friedli <i>et al.</i> (Gold- schmidt)	Quaternary fatty acid (C ₆ –C ₂₂) amino alcohol esters of methylethanol isopropanolamine (HEIPA)	Improved biodegradability; as effective as the conventional dialkylammonium
U.S. 6287545 (2001)	Su (Colgate- Palmolive)	Combination of low HLB (2–9) and high HLB (10–19) ethoxylated branched fatty alcohol ethers or esters as stabilizers; emulsion has a pH 2.0–5.5	Improved freezing and freeze-thaw stability; leave-in or rinse-off
U.S. 6235275 (2001)	Chen <i>et al.</i> (Unilever)	0.1–10% cationic surfactant capable of forming lamellar dispersion; 0.5–30% oil; 0.1–20% silicone surfactant	Improved wet and dry combing and leave a soft dry feel; easy to rinse out
U.S. 6149899 (2002)	Pyles (Helene Curtis)	(a) C ₁₆ –C ₂₂ monoalkyl quat; (b) C ₁₆ –C ₂₂ dialkyl quat; (a)/(b) ≥ 4.0; 1–4% fatty alcohol	Low solid formulation providing substantial conditioning benefits with compromising viscosity to users
U.S. 6147038 (2000)	Halloran (Dow Corning)	Aminofunctional silicone microemulsions having at least one long-chain quaternary amine salt	Optically clear hair conditioner; increased beneficial effects

(continued)

TABLE 10.5 (Contd.)

Patent no. and year	Inventor(s) and company	Technology	Claimed benefits
U.S. 5989533 (1999)	Deegan <i>et al.</i> (Revlon)	0.1–20% cationic conditioning agent; 0.1–20% ester of α - or β -hydroxyl acids; 0.1–30% fatty alcohol; 0.001–10% nonionic surfactant	Improved substantive conditioning, shine, body, combing, and fullness; no greasy or tacky feel
U.S. 5750097 (1998)	Leidreiter <i>et al.</i> (Goldschmidt)	Diacetyl tartrate esters of C ₈ –C ₁₈ fatty acid glycerides	A conditioning agent for hair rinses and conditioning shampoos
U.S. 5616758 (1997)	McCarthy <i>et al.</i> (Karlshamns)	Cationic quaternary aminosilicones	A substantive conditioning agent suitable for a variety of environments such as skin and hair conditioner, fabric softener, and fiber lubricant
U.S. 5552137 (1996)	Manning (Witco)	$(R^1)(R^2)N^+(CH_2CH_2OC(O)R)_2X^-$ wherein R ¹ is C ₁ –C ₆ alkyl, or C ₁ –C ₆ hydroxyalkyl; R ² is C ₁ –C ₆ alkyl, or benzyl; R is C ₁₂ –C ₂₂ alkyl having 0–3 C=C, provided that at least 2 different chain lengths R are present and 0, 1, and 2 C=C are present	A biodegradable conditioning agent; exhibit exemplary performance as a conditioner
U.S. 5393452 (1995)	Raleigh <i>et al.</i> (General Electric)	High-molecular-weight, high-viscosity silicone-polyether copolymer	Improved antistatic properties; conditioning shampoo
U.S. 5334376 (1994)	Robbins <i>et al.</i> (Colgate-Palmolive)	Particulate barium sulfate combined with one or more coreactants from the following groups: silicone free of amino group, long-chain fatty alcohol, long-chain fatty acid amide	Improved body, manageability, and style retention to hair

U.S. 5332569 (1994)	Wood <i>et al.</i> (Alberto-Culver)	Silicon oil in an organic solvent-based carrier comprising PEG and an anionic-cationic emulsifier complex formed from: anionic (phosphate or sulfate) copolymer of dimethylpolysiloxane (20–40 units) and polyoxyethylene (3–15 units) and cationic conditioning compound having at least one quaternary nitrogen or amido amine and one hydrophobic aliphatic or silicone polymer chain	Improved stability of silicone emulsion
U.S. 5213793 (1993)	Moses <i>et al.</i> (Gillette)	$\leq 1\%$ solid; 0.01–0.5% cationic conditioning agent; 5–10% volatile oil; $\leq 3\%$ hydrophobic emulsifying agent	Rinse-on or leave-in; no visible residual by a leave-in application
U.S. 5120531 (1992)	Wells <i>et al.</i> (Procter & Gamble)	0.2–20% hair styling polymer; 0.2–20% nonaqueous solvent; 0.05–25% conditioning agent	Rinse-off conditioner; styling + conditioning
U.S. 5100657 (1992)	Ansher-Jackson <i>et al.</i> (Procter & Gamble)	A mixture of conditioning agents: silicone, cationic surfactant, and fatty alcohol; nonionic long-chain alkylated cellulose ether as the primary thickener; water-insoluble surfactant as a secondary thickener	Provide cleaner hair conditioning; does not have the dirty hair feel and quick resoiling of hair associated with quaternary ammonium
U.S. 4978526 (1990)	Gesslein <i>et al.</i> (Inolex Chem)	Alkyl or alkylamido dimethyl 2,3-dihydroxypropyl ammonium	Clear and stable formulations; do not leave buildup on hair

(continued)

TABLE 10.5 (Contd.)

Patent no. and year	Inventor(s) and company	Technology	Claimed benefits
U.S. 4973476 (1990)	Krzysik (Dow Corning)	Volatile silicone; a functional silicone	Leave-in conditioner
U.S. 4940576 (1990)	Walsh (Chesebrough- Pond's)	A lyotropic liquid crystal phase formed by oppositely charged polymer and surfactant upon dilution	Rinse-on conditioner; more effective on improving the ease of wet combing than a complex not in the form of a liquid crystal
U.S. 4913828 (1990)	Caswell <i>et al.</i> (Procter & Gamble)	Ion pair/wax composites formed by alkyl amine and anionic surfactant	Effective conditioning agent for rinse-off conditioner and fabric conditioners
U.S. 4886660 (1989)	Patel <i>et al.</i> (Colgate- Palmolive)	C ₁₄ –C ₂₂ alkyltrimethyl quaternary ammonium, C ₁₄ –C ₂₂ alkanol, cellulose polymer, copolymer of PVP/VA	Provide shiny, smooth, manageable hair, ease to comb, easy to style, long holding power
U.S. 4868163 (1989)	Takeiet (Kao)	Monoalkyl phosphate having a β -branched alkyl group	Highly safe; transparent or semitransparent jelly-like composition; good moisturizing effect
U.S. 4726945 (1988)	Patel <i>et al.</i> (Colgate- Palmolive)	Distearyl or ditallow quaternary ammonium; C ₈ –C ₁₈ amido C ₂ –C ₃ alkyl di-C ₁ –C ₂ alkylamine; C ₁₄ –C ₁₈ alcohol; mineral oil; cyclomethicone; propylene glycol	Easy to wash out with SLES-based shampoos; provide softness, shine, ease of combing, flyaway control, and manageability; rinse-off conditioner
U.S. 4725433 (1988)	Matravers (Neutrogena)	0.5–3% Laureth-4; 1–4% Choleth-24; 0.1–0.8% hydroxyethylcellulose; 0.4–0.8% Polyquaternium 10	Free of oil and fatty alcohol; nonirritating; no buildup

U.S. 4719104 (1988)	Patel (Helene Curtis)	0.25–4% static-reducing agent; 0.05–1% cationic film-forming polymer; 0.25–4% distearyldimethylammonium; static-reducing agent/cationic polymer = 2:1–20:1	Rinse-on; reduce static
U.S. 4714610 (1987)	Gerstein (Revlon)	Amine oxide; acid to provide a pH of 2.4–3.8	Rinse-on
U.S. 4659565 (1987)	Smith <i>et al.</i> (Ethyl Corp.)	Di C ₆ –C ₁₈ alkyl methylamine oxide	Improve hair body and flyaway reduction
U.S. 4610874 (1986)	Matravers (Neutrogena)	0.1–6% ethoxylated/acetylated lanolin derivative; 0.1–1% ionic polymer; 0.5–1% hydroxyethyl cellulose	A clear freely pourable conditioner
U.S. 4551330 (1985)	Wagman <i>et al.</i> (Helene Curtis)	Oil-in-water emulsion inverts to water-in-oil emulsion at the hair surface when being rubbed onto the hair; unctuous oleaginous; water-dispersible polyvalent metal salt having a cation selected from Al ³⁺ , Ce ³⁺ , F ³⁺ , Zr ⁴⁺ , and aluminum zirconium coordination complex; acid or alkali to give pH 1.5–7.5	Rinse-on or rub-on
U.S. 4275055 (1981)	Nachtigal <i>et al.</i> (Conair)	2.5–7.5% stearamidopropyl dimethylbenzylammonium chloride; 2–5% stearyl dimethylbenzylammonium chloride; 0.25–0.75% NaCl	Conditioning agents also function as pearlizing agents to form a stable pearlescent conditioner

ingredients and compositions has been claimed. More applications on the use of conditioning agents in conditioning (two-in-one) shampoos are discussed in Section III.C.

C. Other Common Auxiliary Ingredients in Shampoos and Conditioners

1. Emulsifying Agents

Most conditioning products are oil-in-water emulsions requiring emulsifying agents for stability. As discussed above, fatty alcohols in combination with quats can confer stability on emulsions of this type. If necessary, other emulsifiers may also be added to improve stability [61,62]. Many emulsifiers used in conditioners are nonionic, including fatty alcohols, ethoxylated fatty alcohols, ethoxylated fatty esters, and ethoxylated sorbitan fatty esters [63].

Many silicones used in hair care products are insoluble in water and must therefore be stabilized in emulsions. To make the manufacturing process easier, many suppliers offer silicones as preformed emulsions.

2. Viscosity/Rheological Modifiers

A sufficiently high product viscosity, usually between 2,000 and 5,000 cP for a shampoo and 3,000 and 12,000 cP for a conditioner, is an important requirement for consumer acceptability.

Salts are the least expensive ingredients to thicken shampoos. The two most commonly used salts are sodium and ammonium chlorides. Salts increase the viscosity of the products by interacting with the long-chain surfactants, converting the small spherical micelles of the surfactants into larger aggregates or even liquid crystal structures [3]. It should be noted that viscosity of a system generally reaches a maximum during salt addition; adding more salt after this point results in a viscosity decrease [3,64].

Alkanolamides, betaines, and amine oxides build viscosity in shampoos by increasing structure (Sections II.A.2(a) and Section II.A.2(b)). This is the same mechanism by which shampoos are thickened by salts [3,4].

Polymeric gums are also important compounds for building viscosity in shampoos and conditioners. They are easily dispersed in water at common use levels of 0.5 to 1.5%. The most commonly used cellulose polymer is hydroxyethylcellulose, which is compatible with anionic and cationic surfactants and stable over a wide pH range [24]. Other cellulose polymers in use include methylcellulose and hydroxypropylmethylcellulose.

Associative thickeners, such as PEG-55 propylene glycol oleate and PEG-120 methyl glucose dioleate, have been employed in shampoos to not only thicken but also introduce advantageous rheological properties [65,66]. These materials

combine the properties of surfactant and polymer in one molecule. They tend to self-associate or interact with other solids in the formula and form a shear-sensitive network structure.

Synthetic polymers are also effective thickeners. These materials produce plastic rheological properties, imparting a yield value to the continuous phase that helps to suspend permanently oil droplets, thus providing excellent stability against creaming or coalescence during storage [67]. The shear-thinning structures they produce can permit easy dispensing of the product from its container.

Examples of synthetic polymers include crosslinked acrylate copolymers (carbomers) [67–69] and modified acrylate derivatives (acrylates/alkylacrylate crosspolymers) [70].

For conditioners, as discussed previously in Section II.B.1, mixtures of fatty alcohols and quaternary ammonium compounds form liquid crystals and gel networks that can greatly increase viscosity.

It should be noted that the use of different thickening agents in shampoos and conditioners can result in varying rheological characteristics, which affects the choice of a particular thickening agent.

3. Foam Modifiers

An important reason besides cleaning for using combinations of primary and secondary surfactants is to improve the quality and volume of foam. As discussed in Section II.A.2, some secondary surfactants such as betaines, amine oxides, and fatty alkanolamides also act as foam modifiers. They change the foams from a loose lacy structure generated by lauryl and laureth sulfates to rich and creamy foams.

4. Opacifying and Clarifying Agents

Opacity or pearlescence in shampoos and conditioners can be generated by a number of raw materials. Cetyl or stearyl alcohol, ethylene glycol stearate, and glyceryl monostearate are frequently used with alkyl sulfates [3,63]. Recently it has been claimed that behenyl alcohol will provide an improved pearlescent appearance (Table 10.6, U.S. Patent 6,608,011). These materials are incorporated into surfactant solutions above their melting points; they then crystallize upon cooling, producing a pearlescent appearance. The degree of opacity depends on the size, distribution, shape, and reflectance of the precipitated crystals. Table 10.6 lists some patents relating to pearlescent shampoos.

In cases where clearness is desired, solubilizing agents are used to improve and stabilize the clarity of a shampoo. Typical clarifying agents include ethanol, isopropanol, propylene glycol, butylene glycol, and sorbitol. Phosphates and short-chain polyethoxylated alcohols and esters have also been used [63].

TABLE 10.6 U.S. Patents Related to Pearlescent/Opacified Shampoos

Patent no. and year	Inventor(s) and company	Technology	Claimed benefits
U.S. 6608011 (2003)	Patel <i>et al.</i> (Colgate-Palmolive)	Behenyl alcohol	Improved pearlescence and stability
U.S. 6365168 (2002)	Ansmann <i>et al.</i> (Henkel)	Dialky ether having C ₁₂ –C ₂₂ linear or branched alkyl and/or alkenyl; Cationic polymer	Mild and excellent conditioning properties; brilliant pearlescence; very good stability
U.S. 6309628 (2001)	Ansmann <i>et al.</i> (Henkel)	Dialky ether having C ₁₂ –C ₂₂ linear or branched alkyl and/or alkenyl; silicone	Synergistic improvement in pearlescent effect and conditioning properties; capable of stabilizing silicones in aqueous formulations
U.S. 6165955 (2000)	Chen <i>et al.</i> (Rhodia)	Fatty acid-based compound	Mild, cold pearlizing concentrate; good high-temperature stability
U.S. 6106816 (2000)	Hitchen (Chesebrough-Pond's)	Insoluble, nonvolatile silicone; suspending polymer; titanium dioxide-coated mica	Improved stability for silicone and pearlizing particles
U.S. 5925604 (1999)	Chen <i>et al.</i> (Rhodia)	Cold pearlizing concentrates do not require CDEA for stabilization and heat for making	Ultramild and CDEA free; energy saving cold making process; excellent pearlescent effects and cleaning
U.S. 5562898 (1996)	Dowell <i>et al.</i> (Helene Curtis)	Long-chain amine ($\geq C_{16}$) or fatty amidoamine ($\geq C_{13}$), and an acid	Excellent opaque or pearlescent aesthetic properties; resist phase separation
U.S. 5529721 (1996)	Salka <i>et al.</i> (Henkel)	Liquid pearlizing composition: alkyl polyglycoside, glycol distearate, and betaine	Easier processing

(continued)

TABLE 10.6 (Contd.)

Patent no. and year	Inventor(s) and company	Technology	Claimed benefits
U.S. 5384114 (1995)	Dowell <i>et al.</i> (Helene Curtis)	Long-chain amine (at least one carbon chain $\geq C_{16}$) or fatty amidoamine ($\geq C_{13}$); neutralized with a suitable acid	A new class of opacifier/pearlizer for water-based compositions; good stability and suspending ability
U.S. 4741855 (1988)	Grote <i>et al.</i> (Procter & Gamble)	Better suspending agents: long-chain esters of ethylene glycol, esters of long-chain fatty acids, long-chain amine oxides	Better suspending stability
U.S. 4654207 (1987)	Preston (Helene Curtis)	Fatty acid ester derived from a C_{16} – C_{22} fatty acid and a saturated C_{14} – C_{22} fatty alcohol; an anhydrous solubilizing agent to presolubilize the ester	Improved capability of making a consistently predictable pearlescence
U.S. 4438096 (1984)	Preston (Helene Curtis)	0.25–1% myristyl myristate	Stable pearlescent shampoo

5. Antioxidants/Free Radical Scavengers

Product stability and performance can be affected by exposure to several oxidative sources, including oxygen, free radicals, UV radiation, oxidative enzymes, catabolic oxidation, and chemical oxidation. Many antioxidants are also good UV absorbers due to their conjugated chemical structure. Typical antioxidants found in cosmetic products are flavonoids, polyphenols, carotenoids, thiols, tocopherol (vitamin E) and ascorbic acid (vitamin C) [71,72]. According to Black [73], a combination of antioxidants from different classes is more effective than a single antioxidant due to an antioxidant cascade mechanism.

6. Photofilters/UV Absorbers

UV absorbers have been used in shampoos for many years and mainly serve to improve color stability against prolonged sunlight exposure in clear packages.

The common UV absorbers available for product protection are benzophenone, methylbenzyleidene camphor, and *para*-aminobenzoic acid (PABA).

Use of UV absorbers or sunscreens in skin care products to prevent photo damage has been widely accepted. The common absorbers for UVB (280 to 320 nm) found in cosmetic products include PABA, salicylic acid derivatives, octocrylene, and phenylbenzimidazole sulfonic acid. Effective UVA (320 to 400 nm) absorbers include methyl anthranilate and avobenzone. Zinc oxide and titanium dioxide can physically block the radiation [74].

The concept of using UV absorbers for hair has been gaining greater attention in recent years. Degradation from UV radiation has been shown to occur in many keratinous materials, including wool [75–77] and hair [78–83]. This process is mediated by oxygen and accelerated by water. Damage to hair from UV exposure includes reduced elastic strength, excessive drying, and discoloration or photo fading of natural or artificial color.

Nonsubstantive photofilters, such as salicylic acid derivatives and octyl methoxycinnamate or benzophenone derivatives, have been included in leave-on formulations for skin and hair. Revlon possesses a patent describing the use of benzophenone and PABA derivatives with cationic surfactants and non-ionic film formers in a mousse for hair protection [84]. L'Oreal has included camphorbenzalkonium sulfate as a proprietary photofilter in hair and skin care formulations [85–92].

Recently a number of cationic photofilters with improved substantivity to hair have been developed for rinse-off products. Croda, Inc. has developed a more substantive cinnamido amine cationic quaternary salt (Crodasome UV-A/B) [93–95]. ISP has also marketed a cationic sunscreen dimethylparamidopropyl laurdimonium tosylate (Escalol HP-610) with improved substantivity and mildness to hair [96].

The combination of a UV filter and antioxidants can provide a greater effect on photo protection since the antioxidants can eliminate free radicals that are generated by the UV light.

7. Sequestrants

Sequestrants can bind Ca or Mg ions present in hard water, thus blocking the formation of insoluble soaps or other salts during washing and rinsing. They can also improve, to a lesser extent, product stability by preventing catalytic decomposition of coloring agents and perfumes in the presence of trace metal ions [97]. Citric acid, EDTA and its salts, and polyphosphates are commonly used sequestrants [63].

8. Preservatives

Preservatives are necessary in products to ensure microbiological robustness. Alkyl sulfates and alkyl ether sulfates, for example, are subject to degradation by

esterases produced by bacteria or fungi at the concentrations normally employed in shampoos. Therefore, a suitable preservative system is required to maintain product stability [13].

Preservatives can be classified into two types: compounds that release formaldehyde and compounds that do not release formaldehyde. Formalin, an aqueous solution of formaldehyde, is a commonly used preservative in shampoos and conditioners [3]. Although formaldehyde has been known as a sensitizer, it is not a problem if used at 0.1% or lower. The use of formaldehyde in baby shampoos is not recommended. Other preservatives that fall in the formaldehyde-releasing group are diazolidinyl urea, imidazolidinyl urea, and DMDM (dimethyloldimethyl) hydantoin.

The most commonly used preservatives that do not release formaldehyde are parabens, quaternium-15, and a mixture of chloromethyl isothiazolinone and methyl isothiazolinone (Kathon CG) [3,63,98,99].

The most frequently used antimicrobials found in commercial shampoos are parabens, methylparaben and propylparaben. Mixtures of different preservatives provide broader protection against a wider spectrum of microorganisms and have been proven to be the most effective method to ensure product robustness [100]. The level of preservative necessary depends on the composition of ingredients, total alcohol level, pH value, and water activity.

Care should be taken in the selection of preservative systems to avoid interaction between preservatives and ingredients or packaging material that could inactivate the preservative, cause product instability, or irritation to skin [101].

9. Fragrances and Colorants

Fragrances and colorants are added to hair care products to mask any undesirable base odor and enhance product aesthetics. These materials can play a crucial role in a consumer's decision to purchase a product on the shelf.

Due to the many oils in fragrances, changes in fragrance may result in dramatic changes in rheological characteristics and phase stability of a formula.

III. TYPES OF SHAMPOOS

A. Cleansing Shampoos

Cleansing shampoos provide basic cleansing of hair. They can be formulated with a variety of primary and secondary surfactants depending on the desired cleaning efficacy and aesthetics of the product (Table 10.7). They usually contain higher levels of anionic surfactants to permit effective cleaning, including removal of substantive residues from styling and other hair care products.

TABLE 10.7 Typical Formula Composition for a Cleansing Shampoo

Ingredient	Activity (%)
Primary surfactants — anionic	8–20
Secondary surfactants/foam boosters — nonionic and amphoteric	0–10
Thickeners — salt, gum, polymer	0–5
Clarifying agents	0–3%
Antioxidants/sequestrants/UV absorbers	0–5
Fragrance, preservative, dye	QS
Water	Balance

B. Mild and Baby Shampoos

The most important requirement for baby shampoos is minimal irritation to scalp, hair, skin, and, especially, eyes. These products are often formulated with levels of nonionic and amphoteric surfactants higher than those found in basic cleaning shampoos.

As mentioned in Section II.A.1(a), the presence of ethylene oxide moieties in alkyl ether sulfates reduces surfactant irritation. Polysorbate 20 and PEG-80, which have 20 and 80 moles of ethylene oxides, respectively, are often incorporated into baby shampoos as anti-irritants. Magnesium salts of these surfactants are also milder than the sodium salts. Table 10.8 shows an example of the formulation of a mild baby shampoo from U.S. Patent 3,928,251. More developments in mild and nonirritating shampoo formulas are listed in [Table 10.9](#).

C. Conditioning (or Two-in-One) Shampoos

Two-in-one shampoos provide conditioning benefits, such as softness, ease of combing, and manageability, in addition to basic cleaning. These products, which were developed in the late 1980s, provide significantly more conditioning than

TABLE 10.8 Formula Example from U.S. Patent 3,928,251 for a Mild Shampoo

Ingredient	Activity (%)
Sodium ethoxylated (3EO) coco sulfate	6.6
Sultaine	4.9
PEG-20 sorbitan monolaurate	14.0
Water	Balance
pH	7.0

TABLE 10.9 U.S. Patents Related to Mild and Nonirritating Shampoos

Patent no. and year	Inventor(s) and company	Technology	Claimed benefits
U.S. 6514918 (2003)	Librizzi (Johnson & Johnson)	Fatty (C ₆ –C ₃₀)amides with EO ₀ –EO ₂₀ or/and PO ₀ –PO ₄₀ groups	Capable of viscosity building and foam boosting without compromising the mildness and safety properties
U.S. 6503873 (2002)	Crudden <i>et al.</i> (Hampshire Chem)	<i>N</i> -acyl ethylenediaminetriacetic acid (ED3A) (Na or K lauroyl)	A novel chelating surfactant product ultra-mild detergent compositions in combination with alkyl sulfates; excellent lather stability
U.S. 6461598 (2002)	O'Lenick <i>et al.</i> (Biosil Res. Ins.)	Salt complexes formed by a fatty ammonium compound and an anionic compound	Extremely mild to the eyes; outstanding conditioning effects; suitable for baby shampoos and body washes
U.S. 6056948 (2000)	Baust <i>et al.</i> (Benckiser NV)	Alkyl polyglycol ether carboxylate with 2–5 EO; alkylether sulfate; Fatty acid amidopropylbetaine	Extra-mild formulation; low tenside concentration
U.S. 6013616 (2000)	Fabry <i>et al.</i> (Henkel)	Monoglyceride (ether) sulfate; fatty acid condensations (isethionates, taurates, or sacrosinates)	Mild detergent mixtures
U.S. 5981450 (2000)	Fabry <i>et al.</i> (Henkel)	Monoglyceride (ether) sulfate; amino acid derivatives (acyl gluamates, vegetable protein hydrolyzates, or vegetable protein fatty acid condensates)	Mild detergent mixtures
U.S. 5968496 (1999)	Linares <i>et al.</i> (Procter & Gamble)	(a) Imidazolinium amphoteric surfactant; (b) polyol alkoxy ester; (a)/(b) = 15:1–1:1	Excellent cleaning performance and mildness; improved foam stability
U.S. 5922671 (1999)	Tracy <i>et al.</i> (Rhodia)	Bis-alkyphenol alkoxyated Gemini surfactants	Improved surfactant properties; mild and environmentally benign

(continued)

TABLE 10.9 (Contd.)

Patent no. and year	Inventor(s) and company	Technology	Claimed benefits
U.S. 5792737 (1998)	Gruning and Weitemeyer (Goldschmidt AG)	Amodipropyl betaines with C7–C12 alkyl group, especially coconut oil fatty acids	Exceptional mild and low irritating properties
U.S. 5756439 (1998)	He <i>et al.</i> (Lever Brothers)	0.1–25 wt% EO/PO polymers: HLB \geq 12, EO portion \geq 50%, mol wt 6,000–25,000; anionic:EO/PO polymer = 1:1–10:1	Significantly enhanced mildness
U.S. 5753600 (1998)	Kamegai <i>et al.</i> (Kao)	Saccharide nonionic surfactant	Low irritation to skin and scalp; improve scalp/skin resistance to external stimuli like antimicrobial contagion; improved antibacterial effect
U.S. 5679330 (1997)	Matsuo <i>et al.</i> (Kao)	C ₆ –C ₃₆ alkylene oxide adduct type	Mild to skin and hair; excellent lathering, detergency, and conditioning effects
U.S. 5514369 (1996)	Salka <i>et al.</i> (Henkel)	Alkyl polyglycosides, betain, and polymeric slip agents	Mild to skin and eyes; more efficient deposition of antidandruff agents; anionic surfactant free; compatible with cationic materials such as conditioners and colorants
U.S. 5478490 (1995)	Russo <i>et al.</i> (Lonza)	Polyglyceryl esters	Meet baby shampoo criteria without the need of using ethylene oxide derivatives; viscosity and clarity can be adjusted by tailoring the polyglyceryl ester
U.S. 5372744 (1994)	Kamegai <i>et al.</i> (Kao)	Alkyl saccharide; sucrose fatty acid ester; anionic and amphoteric surfactants	Low irritation to skin and eyes; creamy and abundant foam; excellent slippery feel
U.S. 5310508 (1994)	Subramanyam <i>et al.</i> (Colgate-Palmolive)	C ₄ –C ₂₄ alcohol EO(1–10) glyceryl sulfonate	Reduced skin irritancy and superior cleaning ability

U.S. 5234618 (1993)	Kamegai <i>et al.</i> (Kao)	0.1–95% saccharide nonionic surfactant; antibacterial agent	High antibacterial effect; restrain the early occurrence of dandruff; does not weaken the cutaneous metabolic and barrier function of the skin
U.S. 5073293 (1991)	Deguchi <i>et al.</i> (Kao)	(a) Alkyl glycoside; (b) dicarboxylic acid; (a)/(b) = 600:1–1:1; (a) + (b) = 1–60%	Excellent foaming power and detergency; easily rinsed out; provides a pleasant feeling to hands during use
U.S. 5035832 (1991)	Takamura <i>et al.</i> (Kao)	Alkylsaccharide nonionic surfactant; silicone derivative	Fine, slippery, creamy foam; very mild to skin and hair; a tense, slippery feeling to the hair; a light, refreshing feeling to the skin
U.S. 4946136 (1990)	Fishlock-Lomax (Amphoterics)	Combination of two amphoteric surfactants (alkylamion or alkoxyalkylamino type, and acylamino type) and one anionic surfactant	Mild shampoos
U.S. 4426310 (1984)	Verunica (Colgate- Palmolive)	Na lauryl ether diethoxy sulfate; polyethoxylated (78EO) glyceryl monoester of coconut oil fatty acids; polyoxyethylene (20EO) sorbitan monooleate; <i>N,N</i> -dimethyl- <i>N</i> -lauryl betaine; disodium lauryl diethoxy sulfosuccinate	Neutral pH and clear; low irritating and does not cause a burning sensation in contact with children's eyes
U.S. 4181634 (1980)	Kennedy <i>et al.</i> (Johnson & Johnson)	C ₁₀ –C ₂₆ alkyleneoxylated (2–3EO) bisquaternary ammonium	Reduced irritant properties of anionic and amphoteric surfactant
U.S. 4154706 (1979)	Kenkare <i>et al.</i> (Colgate- Palmolive)	Amine oxide; alkyl glycoside; polyoxyethylene sorbitan monolaurate; cocoethanolamide; polyacrylamide	Mild nonionic shampoos; free of ionics, allow washing of hair without destroying or adversely affecting the disulfide bonds of the keratin without changing the isoelectric point of the hair
U.S. 3928251 (1975)	Bolich Jr. <i>et al.</i> (Procter & Gamble)	Ethoxylated anionic; zwitterionic (betaines, sultaines); polyethoxylated nonionic	Mild shampoo without stinging eyes

was previously available from shampoos. As such, they represent a major advance in hair care technology (Table 10.10 and Table 10.11).

The primary conditioning agent used in most two-in-one shampoos is dimethicone. Other related silicones have also been used, either in a primary or secondary capacity, including dimethiconol, amodimethicone, and dimethicone copolyol. Because most of these materials are not soluble in water, two-in-one shampoos are generally oil-in-water emulsions, requiring the use of a suitable stabilizer or emulsifying agent.

As stated previously, the surface of chemically treated hair is more negatively charged than that of virgin hair. As a result, hydrophobic conditioning agents like dimethicone bind to treated hair to a lesser extent than to untreated fibers. As a result, some two-in-one shampoos incorporate cationic polymers to increase conditioning on more hydrophilic damaged hair. However, the conditioning performance of cationic polymers in two-in-one shampoos may be no better than dimethicone as a result of formation of complexes in shampoos with high levels of anionic surfactant (Section II.B.3).

It is important to note that cationic quaternary compounds (monoquats) are rarely used alone in two-in-one shampoos because their substantivity to hair is either greatly reduced in the presence of anionic detergents [102] or else they form undesired precipitates with anionic surfactants. Therefore, combinations of anionic, nonionic, amphoteric, and zwitterionic surfactants are often employed to minimize the formation of insoluble complexes.

TABLE 10.10 Formula Example from U.S. Patent 6,007,802 for a Conditioning Shampoo

Ingredient	Activity (%)
ALES (3EO)	14.00
CAP betaine	2.70
Polyquaternium-10	0.15
B8/C10 diester of adipic acid	0.30
Cocamide MEA	0.80
Cetyl alcohol	0.42
Stearyl alcohol	0.18
Carbapol 981	0.50
Dimethicone	1.00
Fragrance	0.70
DMDM hydantoin	0.37
Color solution (ppm)	64
Water and minors	QS to 100

TABLE 10.11 U.S. Patents on Conditioning (Two-in-One) Shampoo Formulas

Patent no. and year	Inventor(s) and company	Technology	Claimed benefits
U.S. 6627184 (2003)	Coffindaffer <i>et al.</i> (Procter & Gamble)	C ₄ –C ₁₆ polyalphaolefin	Improved clean hair feel; improved fullness and body
U.S. 6592856 (2003)	Giles <i>et al.</i> (Unilever)	Combination of conditioning agents: emulsified silicones, cationic polymers, fatty acid polyesters of cyclic polyols and/or sugar derivatives	Improved hair softness and ease of combings, especially for damaged hair, through environmental or harsh mechanical or chemical treatments
U.S. 6506372 (2003)	Dubief <i>et al.</i> (L'Oreal)	Amphoteric polymer with at least one monomeric unit from (meth)acrylate or (meth)acrylamide having at least one fatty chain (C ₈ –C ₃₀)	Improved disentanglement and softness
U.S. 6489286 (2002)	Lukenbach <i>et al.</i> (Johnson & Johnson)	Nonionic/amphoteric/anionic surfactants; at least two conditioning agents selected from cationic celluloses, sugar derivatives, and homopolymers or copolymers	Nonirritating, suitable for children and adults having sensitive skin and eyes; imparts wet and dry detangling, and manageability
U.S. 6436383 (2002)	Murray (Unilever)	Amino-functionalized silicone; emulsified nonamino-functionalized silicone having average particle size $\leq 2 \mu\text{m}$	Improved conditioning performance; softer and more manageable hair
U.S. 6432393 (2002)	Bergmann <i>et al.</i> (Helene Curtis)	Elastomeric resinous material	Increase in hair body without scarifying conditioning attributes
U.S. 6387855 (2002)	De La Mettrie (L'Oreal)	Hydrophobic guar (galactomannan) gum	Improved suspending stability of silicone; good detergent and foaming properties; very good homogeneity and viscosity

(continued)

TABLE 10.11 (Contd.)

Patent no. and year	Inventor(s) and company	Technology	Claimed benefits
U.S. 6375939 (2002)	Dubief <i>et al.</i> (L'Oreal)	Amphoteric polymer with at least one monomeric unit from (meth)acrylate or (meth)acrylamide having at least one fatty chain (C ₈ –C ₃₀)	Improved deposition of antidandruff agent; improved softness and disentangling of the hair
U.S. 6335024 (2002)	Philippe <i>et al.</i> (L'Oreal)	Aminoalcohol derivatives containing a urea functional group	A conditioning agent for hair and a moisturizing agent for skin
U.S. 6306805 (2001)	Bratescu <i>et al.</i> (Stepan)	Anionic–cationic bridging surfactant blends; bridging surfactants selected from ethoxylated alkanolamide, semipolar nonionic, amphoteric, zwitterionic	Clear solutions at a variety of concentrations in water; impart cleaning, foaming, and conditioning properties to hair
U.S. 6264931 (2001)	Franklin <i>et al.</i> (Akzo Nobel)	≤4% fatty aliphatic (C ₁₁ –C ₂₄) quaternary ammonium having ester linkages	Comparable with anionic surfactants; biodegradable conditioning agent
U.S. 6162423 (2000)	Sebag <i>et al.</i> (L'Oreal)	Dialkylether with C ₁₂ –C ₃₀ alkyl radicals, same or different, linear or branched, saturated or unsaturated	Improved homogeneity and stability of silicone; sufficient foaming power
U.S. 6156297 (2000)	Maurin <i>et al.</i> (L'Oreal)	Nonvolatile vegetable oil as a conditioning agent; anionic sulfate/alkyl glycoside ≤2	Excellent cosmetic properties: disentangling, softness, sheen, and body of the hair; good washing and foam power
U.S. 6110450 (2000)	Bergmann (Helene Curtis)	Ceramide and/or glycosceramide and phytantriol	Especially advantageous wet disentangling; synergistic effect
U.S. 6106816 (2000)	Hitchen (Chesebrough-Pond's)	Suspending polymer (e.g., polyacrylic acid, carylates copolymer) for silicones; titanium dioxide-coated mica	Improved phase/suspending stability

U.S. 6051214 (2000)	Isbell <i>et al.</i> (U.S. Secretary of Agriculture)	Fatty acid estolides	Enhanced rinseability, wet feel, detangling, dry comb feel, style management, shine and/or body to the hair
U.S. 6051213 (2000)	Beauquey <i>et al.</i> (L'Oreal)	At least 2 wt% alpha-hydroxylated carboxylic acids and their derivatives	Enhanced lightness, smoothness, shine, and mechanical strength
U.S. 6048519 (2000)	Hiraishi <i>et al.</i> (Helene Curtis)	A particular combination of silicone compounds; silicone gum with a viscosity of ≥ 1 MP; silicone fluid with viscosity of ≤ 100 kP; amino-functionalized silicone	Excellent conditioning benefits
U.S. 6007802 (1999)	Coffindaff <i>et al.</i> (Procter & Gamble)	Ethoxylated alkyl sulfate; amphoteric surfactant; insoluble conditioning agent; cellulosic cationic polymers; synthetic esters	Excellent cleaning performance and improved conditioning; minimum buildup
U.S. 5997854 (1999)	von Mallek (Henkel)	Quaternary ammonium; amphoteric and anionic surfactants; alkyl polyglycoside	Enhanced conditioning in the absence of silicones
U.S. 5990059 (1999)	Finel <i>et al.</i> (Helene Curtis)	0.01–10 wt% microemulsion of high viscosity, slightly crosslinked silicone with a particle size of ≤ 0.15 μm ; 0.01–10 wt% cationic deposition polymer	Excellent mechanical stability; excellent conditioning ability; high optical transparency or translucency
U.S. 5980877 (1999)	Baravetto <i>et al.</i> (Procter & Gamble)	Nonvolatile conditioning agent having a dual particle size range of 2 μm and 5 μm	Excellent cleaning in combination with improved conditioning; minimize adverse side effects associated with excess buildup
U.S. 5977038 (1999)	Birtwistle <i>et al.</i> (Helene Curtis)	Cationic conditioning polymer having a charge density of $\leq +3.0$ meq/g	Selectively enhances the wet feel and ease of wet comb, while reducing the ease of dry combing to allow an easy styling
U.S. 5888489 (1999)	von Mallek (Henkel)	Quaternary ammonium, amphoteric, and anionic surfactants, alkyl polyglycoside, emollient, amide	Enhanced conditioning in the absence of silicones

(continued)

TABLE 10.11 (Contd.)

Patent no. and year	Inventor(s) and company	Technology	Claimed benefits
U.S. 5776871 (1998)	Cothran <i>et al.</i> (Procter & Gamble)	An insoluble silicone stably suspended with a low level of cationic polymer	A stable conditioning antidandruff shampoo without the need for crystalline suspending agents or polymeric thickening agents; do not need the costly heating and cooling steps
U.S. 5747436 (1998)	Petal <i>et al.</i> (Colgate-Palmolive)	Anionic and amphoteric surfactants; complex acid:amine (1:1 mole ratio); mixture of monoalkyl and dialkyl ammonium	Improved antistatic properties; free of silicone
U.S. 5733536 (1998)	Hill <i>et al.</i> (Whithill Oral Tech.)	Ultramulsion comprises: a dispersed silicone with particle size of 0.1–10 μm , viscosity $1.5\text{--}4 \times 10^6$ cP, a EO/PO copolymer surfactant with mol wt 1,100–150,000; surfactant/silicone = 400:1–1:2	Method for making the ultramulsion; distinctive conditioning, moisturizing, protecting, etc.; the silicone phase functions as a reservoir for various treatment substances
U.S. 5726137 (1998)	Petal <i>et al.</i> (Colgate-Palmolive)	1–16% long-chain ($\text{C}_{24}\text{--}\text{C}_{50}$) aliphatic alcohol with 0–40 EO; an alkyl amine having a pK_a of at least 7.5; a water-soluble, film-forming polycationic polymer	A low-silicone conditioning shampoo has a high degree of conditioning properties; a nonsilicone conditioning shampoo possesses a high degree of styling control properties
U.S. 5665267 (1997); U.S. 5587154 (1996)	Dowell <i>et al.</i> (Helene Curtis)	Long-chain fatty ($\geq \text{C}_{16}$) amine; water-insoluble hair-treating compounds (silicones, antidandruff agent); suitable acid	Improved suspending ability without a thickening agent; effectively cleanse hair and deliver hair-treating compounds
U.S. 5656258 (1997)	Cauwet <i>et al.</i> (L'Oreal)	A mixture of conditioning polymers: (a) quaternary polyammonium polymer and (b) polymer containing 70–90 wt% diallyldialkylammonium units, (a)/(b) ≤ 1.0	Improved the disentanglement of hair (especially wet hair) and the softness of the hair and skin; reduced buildup after repeated applications

U.S. 5641480 (1997)	Vermeer (Lever Brothers)	Heteroatom containing alkyl aldonamides and conditioning agents	Enhanced stability and viscosity; improved foam and clarity; improved conditioning characteristics
U.S. 5612025 (1997)	Cauwet-Martin <i>et al.</i> (L'Oreal)	Mixture of conditioning polymers: a quaternary polyammonium polymer with mol wt $\leq 100,000$, a polymer with 70–90% C ₁ –C ₁₈ diallyldialkylammonium units and 30–10% acrylic or methacrylic units	Synergistic cosmetic effect; improved softness of hair and skin; improved disentangling
U.S. 5580494 (1996)	Sandhu <i>et al.</i> (Colgate-Palmolive)	High charge density (>200) cationic polymers with anionic surfactants	Improved stability; reduce the use of water-insoluble silicone; less harsh to hair protein
U.S. 5415857 (1995)	Robbins <i>et al.</i> (Colgate-Palmolive)	0.3–5% aminosilicone; 0.1–5% cationic surfactant conditioning agent	Improved hair conditioning characteristics; reduced buildup after repeated applications
U.S. 5346642 (1994)	Patel <i>et al.</i> (Colgate-Palmolive)	Long-chain (C ₂₅ –C ₄₅) saturated primary alcohol or a derivative	Improved emulsion stability; desirable pearlescent appearance; improved hair conditioning effect
U.S. 5213716 (1993)	Patel <i>et al.</i> (Colgate-Palmolive)	Long-chain (C ₂₅ –C ₄₅) saturated primary alcohol or a derivative	Improved emulsion stability; desirable pearlescent appearance; improved hair conditioning effect
U.S. 5211883 (1993)	Yamashina <i>et al.</i> (Kao)	Amidoamine type amphoteric surfactant; silicone polymer	Excellent soft and smooth feeling during washing and rinsing; superb natural hair-set effect; no oily stickiness and roughness; easy passage of comb through the hair; mild to skin, eyes, and mucous

(continued)

TABLE 10.11 (Contd.)

Patent no. and year	Inventor(s) and company	Technology	Claimed benefits
U.S. 5145607 (1992)	Rich (Takasago)	Anionic surfactants (Na, K, NH ₄ alkyl sulfate); cationic conditioning surfactant	Clear conditioning shampoo
U.S. 5106613 (1992)	Hartnett <i>et al.</i> (Colgate- Palmolive)	C ₆ /C ₈ /C ₁₀ alkyl and alkyl lower alkoxyated sulfates; aminosilicones; microcrystalline waxes	Better conditioning properties than detergents that contain longer chain alkyl groups
U.S. 4997641 (1991)	Patel <i>et al.</i> (Colgate- Palmolive)	Poly-lower alkylene (e.g., polyethylene and polypropylene); hydrocarbon solubilizer	Improved wet and dry combing, manageability; reduced static charge and flyaway
U.S. 4997641 (1991)	Hartnett <i>et al.</i> (Colgate- Palmolive)	C ₆ /C ₈ /C ₁₀ alkyl and alkyl lower alkoxyated sulfates	Improved hair conditioning properties; reduced buildup after repeated applications
U.S. 4741855 (1988)	Grote <i>et al.</i> (Procter & Gamble)	Long-chain acyl derivatives: long-chain esters of ethylene glycol, esters of long-chain fatty acid, long-chain amine oxides	Stable silicone-containing shampoo
U.S. 4728457 (1988)	Fieler (Procter & Gamble)	Heated premixes (silicone) are added to a main mix (surfactants and suspending agents) at ambient temperature	Improved process for making silicone-containing shampoos
U.S. 4704272 (1987)	Oh <i>et al.</i> (Procter & Gamble)	Tri long-chain alkyl quaternary ammonium, or tri long-chain amine; nonvolatile silicone	Good hair conditioning and stable products

Conditioning from two-in-one shampoos is expected to occur primarily at the rinsing stage during which time the shampoo emulsion breaks, releasing the silicone for deposition on hair. This separation of cleaning and conditioning stages permits the shampoo to perform efficiently both of its functions: removal of soils and deposition of conditioning agents.

D. Antidandruff Shampoos

In the U.S. hair care products containing an antidandruff ingredient are considered as over-the-counter (OTC) drugs. However, different regulations are applied in other regions. An antidandruff shampoo is treated as a quasi-drug in Japan, a therapeutic product in Australia, and may be a cosmetic or an OTC product in Europe, depending upon the claims.

Water-insoluble anti-inflammatory agents or antidandruff particulates are more effective than water-soluble particulates. This is because antidandruff particulates come out of suspension when diluted by application to wetted hair, and deposit on the hair and scalp. When the composition is rinsed from the hair, many particulates of the agent remain on the hair and scalp to provide an effective amount for treatment. A soluble agent is washed away for the most part during rinsing, providing only an ineffective amount remaining on the scalp.

Water-insoluble antidandruff agents, such as zinc pyrithione, selenium sulfide, climbazole, coal tar derivatives, and powder sulfur, have been used in many products for treating dandruff (Table 10.12). Although these materials are effective in controlling dandruff, several difficulties can occur in formulating these materials into a stable product. In general, most of these ingredients have high specific density, which makes it hard to suspend them in liquid shampoos. Selenium sulfide is also sensitive to pH, and begins to break down and form toxic sulfides during storage when the pH becomes greater than 6.5.

A great deal of work in formulating antidandruff shampoos has been performed in the past decade (Table 10.13), resulting in claims of improved

TABLE 10.12 Antidandruff Agents for Shampoos [2]

Ingredient	Concentration (%)
Zinc pyrithione	1.0–2.0
Climbazole	0.1–2.0
Selenium sulfide	0.1–4.0
Salicylic acid	1.5–3.0
Powder sulfur	2.0–5.0
Coal tar derivatives	0.5–5.0

TABLE 10.13 U.S. Patents on Shampoo Formulas with Antidandruff Efficacy

Patent no. and year	Inventor(s) and company	Technology	Claimed benefits
U.S. 6663875 (2003)	Glauder <i>et al.</i> (Clariant)	Oxiconazole (Z-1-(2,4-dichlorophenyl)-2-(1H-imidazol-1-yl)-O-(2,4-dichlorobenzyl)ethanone oxime and salt)	Broad antimicrobial spectrum and low toxicity; free of cytotoxic agents
U.S. 6649155 (2003)	Dunlop <i>et al.</i> (Procter & Gamble)	0.02–5% cationic guar gum derivative (mol wt from 50,000 to 700,000, charge density from 0.05 to 1.0 meq/g); 0.1–4% antidandruff particulate (pyridinethione salts, selenium sulfide, or sulfur); nonvolatile conditioning agent	Improved coacervate formed between the cationic polymer and anionic surfactant upon dilution of the shampoo; superior combination of antidandruff efficacy and conditioning (three-in-one)
U.S. 6515007 (2003)	Murad	Acidic component of a hydroxy acid or tannic acid or salts in combination with vitamin E component and an antigrowth agent for the antidandruff effect, or with niacin component and a 5- α reductase inhibitor for the antihair-thinning effect	Antidandruff; antihair thinning (three-in-one)
U.S. 6514490 (2003)	Odds <i>et al.</i> (Janssen Pharmaceutica)	Ergosterol biosynthesis inhibitor; 10'-undecen-3-oyl-aminopropyl trimethylammonium methylsulfate	Effective antifungal and antidandruff composition
U.S. 6451300 (2002)	Dunlop <i>et al.</i> (Procter & Gamble)	0.005–1.5% polyalkylene glycol; nonvolatile conditioning agent; cationic polymer	Superior combination of antidandruff efficacy and conditioning (three-in-one)

U.S. 6410593 (2002)	De Mesanstowne <i>et al.</i> (CECA)	1.5–3.5% Amphoram U (undecylenamidopropylbetaine, an amphoteric surfactant)	A multifunctional amphoteric surfactant serves as a cleaning and foaming agent and an antifungal agent to treat or prevent dandruff
U.S. 6333027 (2001)	Hopkins <i>et al.</i> (Johnson & Johnson)	0.1–15% active ingredient selected from undecylenic acid, undecylenamidopropylbetaine, and mixtures thereof	A composition for treating and/or ameliorating dandruff, seborrheic dermatitis, psoriasis, and eczema; nonstinging to the eyes
U.S. 6323166 (2001)	Kamiya (Kamiya)	0.05–5% essential oil selected from terpene esters and terpene hydrocarbons; 3–20% <i>N</i> -acylamino acid salt; 0.1–15% sucrose fatty acid ester or C ₆ –C ₁₈ fatty acid alkylolamide	Softens the hair and give a rinsing effect and controlling dandruff and itch on the scalp; remove minute chemicals deposited on the skin responsible for atopic dermatitis
U.S. 5900393 (1999); U.S. 5834409 (1998)	Ramachandran <i>et al.</i> (Colgate- Palmolive)	Climbazole or a mixtures of climbazole and one or more cotherapeutics such as salicylic acid; ratio of amphoteric to anionic surfactant from 0.75 to 1.25	Mild detergent composition; therapeutic effect on scalp disorders (itch, irritation, and dryness) encountered in warm weather and in tropical regions
U.S. 5723112 (1998)	Bowser <i>et al.</i> (Chesebrough- Pond's)	Metal pyrithione with at least 90% of particles ≤5 μm; water-soluble cationic polymer as a deposition aid	Improved mechanical stability; excellent antidandruff ability
U.S. 5624666 (1997)	Coffindaffer <i>et al.</i> (Procter & Gamble)	0.1–5% particulate antidandruff agent having an average particle size from 0.35 to 5 μm; 0.01–1% soluble cationic polymer as a stabilizing agent	Suspend without crystalline suspending agents or hydrophilic polymeric thickeners; have good, nonslimy feel

(continued)

TABLE 10.13 (Contd.)

Patent no. and year	Inventor(s) and company	Technology	Claimed benefits
U.S. 5302323 (1994)	Hartung <i>et al.</i> (Abbott Lab.)	0.5–2.5% selenium sulfide; two suspending agents: di(hydrogenated) tallow phthalic acid amide and one selected from hydroxypropylmethylcellulose and Mg Al silicate; pH 4.0–6.5 buffer system with Na citrate and citric acid; at least 18% anionic surfactant	Improved pH stability, suspension stability, lathering, and conditioning (three-in-one)
U.S. 5154847 (1992)	LaPetina <i>et al.</i> (Helene Curtis)	Ethylene–maleic anhydride resin or polyacrylic acid resin, and alkanolamide and/or wax ester	Improved suspending stability; improved foaming properties
U.S. 4867971 (1989)	Ryan <i>et al.</i> (Colgate-Palmolive)	0.1–2% 1-imidazolyl-1-(4-chlorophenoxy)-3,3-dimethylbutan-2-one (climbazole); pH 4–5.5	A stable homogeneous liquid antidandruff shampoo; increased deposition of climbazole; enhanced antidandruff efficacy
U.S. 4854333 (1989)	Inman <i>et al.</i> (Procter & Gamble)	0.005–0.9% peroxy oxidizing agent, e.g., hydrogen peroxide and Na percarbonate; 0.1–5% selenium sulfide having average particle size <25 μm	A selenium sulfide shampoo with a neutral pH (no need for a buffer system); improved color stability
U.S. 4379753 (1983)	Bolich (Procter & Gamble)	Metal salt of pyridinethione	Improved product aesthetics

antidandruff efficacy, stability, and mildness. More complicated formulas, called three-in-one shampoos, have been developed to provide additional benefits, such as conditioning, temporary styling, and antihair-thinning, in addition to cleaning and dandruff control.

E. Shampoos with Specific Cosmetic Benefits

Shampoos providing specific cosmetic benefits other than conditioning have been developed and have gained popularity in recent years. Cosmetic benefits such as volume increase, shine increase, ease of styling, moisturizing, replenishing, etc., have been claimed. Table 10.14 lists some examples of shampoo formulas that provide specific cosmetic benefits.

IV. BASIC MECHANISM OF HAIR CLEANING

The primary function of shampoos is to clean hair. In order to assess the effectiveness of different detergents in cleaning various soils, it is important to understand the different cleaning mechanisms operating during the shampooing process.

A. Nature of the Hair Surface

Before discussing specific detergency mechanisms, it is necessary to consider the nature of the hair surface. The structure of hair is described in detail in Robbins' book [3]. Figure 10.1 shows a scanning electron microscopy (SEM) image of the root end of a typical, virgin hair fiber. The fiber consists of a hydrophilic central portion, the cortex, covered by 5 to 10 overlapping layers of cells termed the cuticle [3]. Compared to the cortex, the cuticle contains a large percentage of cystine residues, resulting in a highly crosslinked structure. The surface of the cuticle consists of a monolayer of covalently bound fatty acids that impart a hydrophobic nature to a healthy, undamaged hair fiber [103–105].

An important component of the cuticle structure is the cell membrane complex, or CMC, which consists of a (δ) proteinaceous layer, sandwiched by two (β) lipid layers. The CMC is the only continuous structure in hair. It acts as a cement between different layers or components of the hair fiber and is responsible for the physical integrity of the hair structure.

Recently, a unique anteiso methyl-branched saturated fatty acid of 21 carbons, 18-methyl eicosanoic acid or 18-MEA, was identified in the outermost portion of the epicuticle, which is part of the CMC [104,106–110]. 18-MEA is the predominant fatty acid in the epicuticle. It makes up approximately 40% of the surface lipid layer of wool and human hair [106,107,109]. In addition to 18-MEA, other fatty acids have been isolated in smaller amounts from the epicuticle including

TABLE 10.14 U.S. Patents on Shampoo Formulas with Cosmetic Benefits other than Conditioning

Patent no. and year	Inventor(s) and company	Technology	Claimed benefits
U.S. 6689347 (2004)	Barbuzzi <i>et al.</i> (Unilever)	Water-insoluble particles having a layered structure comprising O atoms and silicone and/or P atoms, and organic functional groups bonded to silicone or P atoms by covalent bonds	Impart body attributes such as root lift, volume, bounce, and manageability in the absence of a styling polymer which leads to stickiness or dry feel
U.S. 6440907 (2002)	Santora <i>et al.</i> (Johnson & Johnson)	0.01–3% humectant (cationically changed polyols, C ₆ –C ₂₂ sugar derivatives)	Exceedingly mild to skin and eyes; leave skin and hair feeling moist but without feeling excessively oily and slippery; good dispersibility and foamability
U.S. 6432393 (2002)	Bergmann <i>et al.</i> (Helene Curtis)	Elastomeric resinous materials having a G' modulus between 1×10^2 and 1×10^5 dyn/cm ²	Increase in hair body without sacrificing conditioning attributes
U.S. 6348439 (2002)	Rousso <i>et al.</i> (Bristol-Myers Squibb)	Nonionic and/or cationic polymers; pH 8–10 when cationic polymer is present; pH 8–14 when cationic polymer is not present	Provide body, fullness, and texture to fine or very fine hair
U.S. 6231843 (2001)	Hoelzel <i>et al.</i> (Wella)	5–50% anionic, nonionic, amphoteric surfactants; 2–10% fruit acids, at least two acids selected from lactic, citric, maleic, tartaric, gluconic, fumaric, and succinic acid; 0.2–2% pantothenol, pantothenic acid, and esters of pantothenic acid	Hair cleaning composition free of oily and greasy ingredients
U.S. 6046145 (2000)	Santora <i>et al.</i> (Johnson & Johnson)	0.01–3% humectant (cationically charged polyols, C ₆ –C ₂₂ sugar derivatives)	Extra mild to skin and eyes; leave skin and hair feeling moist but without feeling excessively oily and slippery; good dispersibility and foamability

U.S. 6024952 (2000)	Story <i>et al.</i> (Andrew Jergens)	Cationic polymer (polyquat-6); anionic emollient (sulfated castor oil)	A sparingly soluble moisturizing complex is formed; the anionic/cationic complex deposits strongly on the hair and is difficult to remove
U.S. 5994280 (1999)	Giret <i>et al.</i> (Procter & Gamble)	3–40% insoluble, nonionic oil or wax or mixture; 0.1–8% C ₁₀ –C ₁₈ fatty acid	Superior physical, viscosity, and foam stability; provide moisturizing effect
U.S. 5858340 (1999)	Briggs <i>et al.</i> (Procter & Gamble)	0.5–20% polyhydric alcohol humectant; water-soluble polyglycerylmethacrylate lubricant; polyethyleneglycol (EO 2–200) glyceryl fatty (C ₅ –C ₂₅) ester; hydrophilic gelling agent	Improved moisturization and skin feel; reduced tack and residue characteristics; excellent visual clarity and absorption characteristics
U.S. 5661189 (1997)	Grieseson <i>et al.</i> (Unilever)	Anionic, cationic, amphoteric, zwitterionic surfactants; thickening agents; benefit agents (silicones, fats and oils, vitamins, plant extracts, sunscreens, alkyl lactate, essential oils, etc.); small amount of soap	Effective and stable detergent system for delivering a wide variety of benefit agents
U.S. 4839162 (1989)	Komori <i>et al.</i> (Kao)	Diglyceride (liquid at room temperature); polyol type humectant and/or hydrophilic humectant	Provide high and long-lasting moisturizing effect; preserve the moisturizing function after a lapse of time
U.S. 4452989 (1984)	Deckner <i>et al.</i> (Charles of the Ritz)	2-Pyrrolidone-5-carboxylic acid and salts	Nonirritant to skin and eye; provide unique moisturizing properties
U.S. 4374125 (1983)	Newell (Helene Curtis)	0.01–1% sodium-2-pyrrolidone-5-carboxylate; 0.05–5% glycerine; 0.05–5% collagen protein	Restore the proper moisture level in initially moisture deficient hair; maintain the proper moisture level in hair initially having a normal moisture content
U.S. 4220168; U.S. 4220166 (1980)	Newell (Helene Curtis)	0.01–1% sodium-2-pyrrolidone-5-carboxylate; 0.05–5% glycerine; 0.05–5% collagen protein	Maintain the proper moisture level in hair initially having a normal moisture content

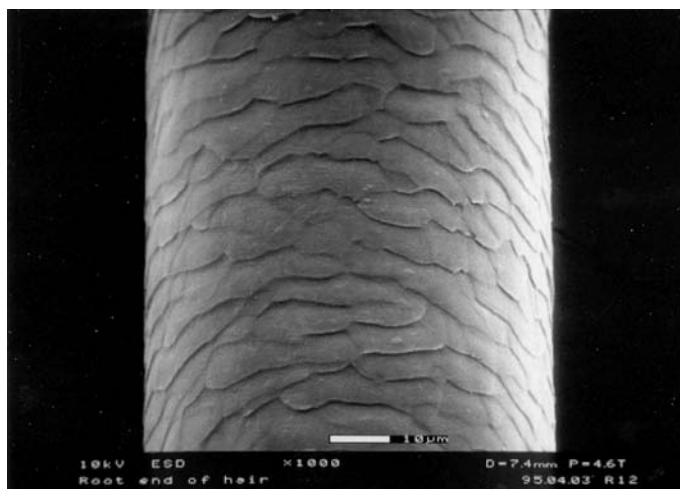
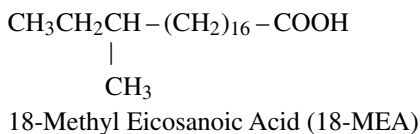


FIG. 10.1 SEM image of a typical root section of a virgin hair fiber.

lauric (C12), myristic (C14), palmitic (C16), oleic (C18:1), stearic (C18), arachidic (C20), behenic (C22), lignoceric (C24), and cerotic (C26) acids [107–110].



Untreated hair comprises proteins that exhibit an isoelectric point near pH 3.67 [111]. As a result, despite its hydrophobic surface, hair carries a negative charge at the normal pH levels of hair care products. Loss and damage of the surface lipid layer also reduce the hydrophobicity of the hair. This combination of negative charge and hydrophobicity affects the types of soils that bind to hair as well as the ease with which different soils can be removed from the fiber surface.

This situation is further complicated by the fact that the concentrations of negative charges increase from the root to the tip of the virgin hair fiber [105,112,113]. This is primarily a result of weathering from sunlight exposure, which oxidizes the hair, converting cystine to cysteic acid and cystine *S*-sulfonate. The tips, being the oldest portion of a hair fiber will have been subjected to the greatest degree of stress and will carry the greatest degree of negative charge.

In addition to surface energy, the physical condition of the hair fiber also affects the types of soils attracted to and removed from the hair surface. [Figure 10.2](#) shows an SEM image of the tip region of a hair fiber. The uplifting at the scale edges

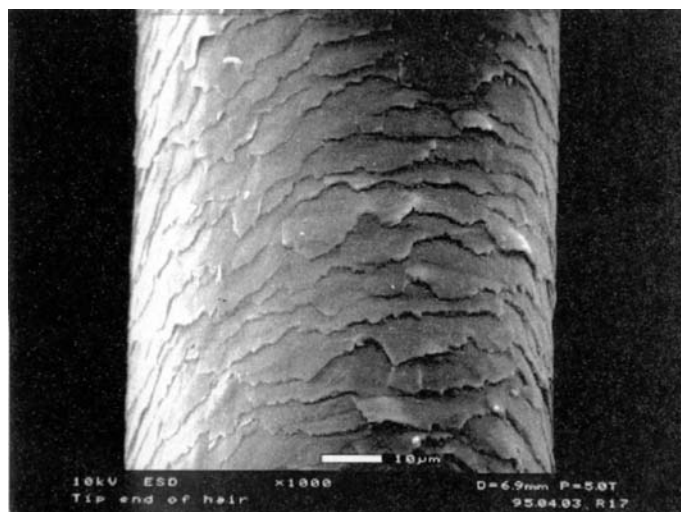


FIG. 10.2 SEM image of the tip end of the same hair fiber as in [Figure 10.1](#).

caused by weathering and grooming exposes normally inaccessible areas in which soils can become physically entrapped.

If hair is further damaged to the point that the cuticle has split ([Figure 10.3](#)), the exposed hydrophilic cortex could strongly adsorb hydrophilic soils that would not bind as strongly to the intact hydrophobic cuticle layers.

B. Cleaning of Particulate Soil

The soil found on hair can be classified into two types: solid particulate and liquid or oily soil. Solid soils can come from hair care products or from the environment. Examples of the former might be polymeric resins or antidandruff agents, while the latter includes airborne particles carried by air currents, dust, carbon particles in the form of soot or clays, or rubber abraded from automobile tires [113–116].

Solid particles usually adhere to the hair surface through van der Waals or ionic forces [116–118]. In water, the ease of removing these soils from a surface depends upon the relative affinities for each other of the water, soil, and substrate. These affinities are expressed as W_a , the work of adhesion, which is defined as the free energy change per unit area involved in removing an adhered solid particle from a surface (in this case the hair fiber) to which it is adhered. In water, W_a can be expressed as

$$W_a = \gamma_{PW} + \gamma_{FW} - \gamma_{PF} \quad (1)$$

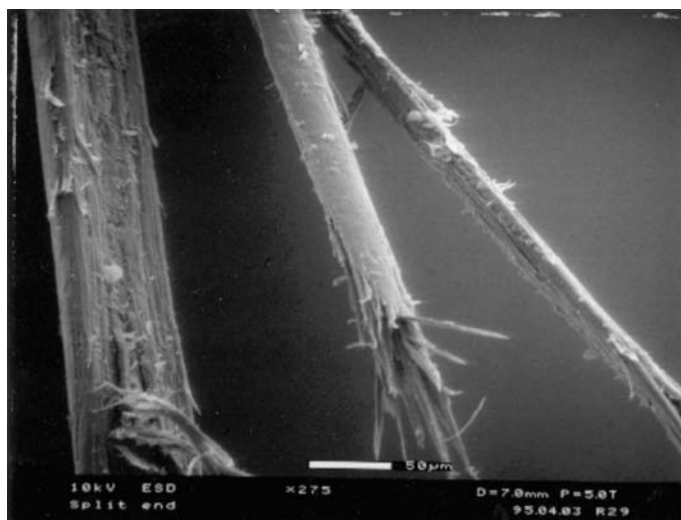


FIG. 10.3 SEM image of a split end.

where γ_{AB} represents the interfacial tension between any two surfaces A and B. In this case, P represents the soil particle, W represents water, and F represents the fiber surface [119].

An examination of the above equation indicates that, in water, hydrophobic particles are quite difficult to remove from a hydrophobic hair surface because such systems result in high values for γ_{PW} and γ_{FW} and low values for γ_{PF} , resulting in a high work of adhesion.

Anionic and nonionic surfactants can reduce the work required to remove solid particles. This is because these surfactants adsorb to hair or hydrophobic soils with their hydrophobic tails in contact with the hydrophobic surfaces and their hydrophilic heads oriented toward the bulk solution. This has the effect of reducing γ_{FW} and γ_{PW} and, thus, W_a . Even more importantly, anionic surfactants remove particulates as a result of the increase of negative potentials on soil and hair upon anionic adsorption to these surfaces. This increases mutual repulsion between particulate and fiber, thus facilitating soil removal.

The ease of removing particulate soil from the hair surface is also dependent upon particle size. As size decreases, the surface area per unit weight of the particle, and consequently the area of actual contact per unit weight between particle and substrate, increases. As a result, more force per unit area is required to remove the particle [120]. In a normal cleaning process, particulates that are less than $0.1 \mu\text{m}$ in size cannot be effectively removed from fibrous substrates [121].

C. Cleaning of Oily Soil

The most important type of oily soil found on hair is sebum, which is produced by the sebaceous glands on the scalp. Sebum is a mixture of fatty materials that is solid at room temperature, but almost completely molten at body temperature [122].

Various mechanisms are involved in removing the oily materials. These include roll-up, emulsification, liquid crystal formation, and solubilization. In the following sections the mechanisms and their relative importance in the hair cleaning process are discussed.

1. Roll-Up Mechanism

Figure 10.4 shows oil droplets adsorbed to a solid substrate. The equilibrium contact angle formed by the droplet is determined by Young's equation

$$\lambda_{FW} = \lambda_{FO} + \lambda_{OW} \cos \theta \quad (2)$$

where λ is the interfacial tension between two phases, O represents the oil phase, W the water phase, and F the fiber, and θ is the contact angle.

According to Eq. (2), the adsorption of a surfactant to the fiber surface (oriented with the hydrophilic head pointing toward the aqueous phase) increases the contact angle, θ , as a result of a reduction in λ_{FW} . If the reduction in λ_{FW} is sufficiently large, the contact angle will increase to 180° , and the oil droplet will spontaneously separate from the fiber surface. At this point, then, the surfactant has increased the affinity of the fiber surface for water to such an extent that the water simply displaces the oil droplet and rolls it up. This process was first described by Adam [123] and by Kling [124] and is termed roll-back.

In practice, a thin film of oily soil can often form on the hair surface with a contact angle of zero. In this case, it may not be possible for a surfactant to roll back completely the hydrophobic soil without additional mechanical action such as rubbing and flexing.

A major hurdle to the roll-back process is high soil viscosity. Applying mechanical work in this case can increase soil removal, as does increasing temperature,

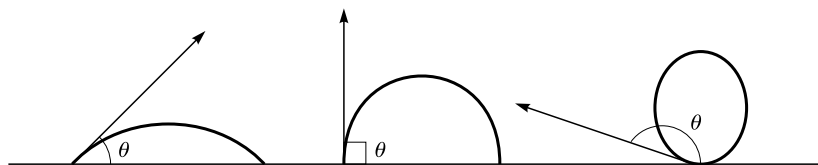


FIG. 10.4 Different stages of the roll-up process. Note the increase in the contact angle as the oil droplet is rolled back from the substrate.

a step that increases rates of diffusion and surfactant adsorption, while reducing viscosity.

2. Micellar Solubilization

Surfactants tend to form colloidal-sized association structures, or micelles, when the concentration is above a particular level termed the critical micelle concentration (CMC). In such structures, the hydrophobic portions of the surfactants are buried in the micelle interior, and the hydrophilic heads are oriented toward the bulk solution [125].

Because of their makeup, micelles can solubilize insoluble soils, such as fatty acids and hydrocarbons, in the hydrophobic interior of the micelle structure. Non-polar soils are incorporated deep in the interior, while more polar materials are found closer to the hydrophilic heads [126,127].

The kinetics by which micelles solubilize fatty acid soils have been described as (1) adsorption of micelles on the soil surface; (2) incorporation of soil into the micelles; and (3) desorption of the soil-containing micelles. Diffusion of micelles to and away from the soil surface precedes and completes this solubilization process [128,129].

Solubilization is particularly important for hair cleansing because under normal shampooing conditions a significant concentration of micelles is expected to be present. Thus, final surfactant concentration in the lather during shampooing has been estimated to be 1 to 2%, a value that is 5 to 10 times the CMC of SLS [1]. This is an important value in view of reports that, for several surfactants, maximum detergency in cleaning of various fats and oils occurs at 6 to 10 times the CMC [130,131].

Addition of salts or other ingredients that shield negative charges decreases repulsion between the charged head groups of ionic surfactants, thus permitting closer packing of the surfactant molecules, leading to larger and rod-like micelles [132–136]. Such a size or shape change increases the volume of the inner core available for solubilizing hydrocarbons and long-chain polar compounds. Some ingredients in shampoos, such as long-chain amides, long-chain fatty alcohols, and betaines, form mixed micelles with the anionic detergents. The formation of mixed micelles also reduces repulsion between ionic head groups and results in larger micelles with more solubilizing capacity. As is the case with roll-up, soil removal by solubilization is greatly enhanced by increasing temperature [137] and application of mechanical work through rubbing and flexing of hair and through rinsing.

More work is needed to determine the exact contribution of solubilization to the cleaning of different soils. However, solubilization is undoubtedly a highly significant cleaning mechanism and, quite likely, is the most important means by which shampoos remove soils from human hair.

3. Emulsification, Penetration, and Mesophase (Liquid Crystal) Formation

Emulsification and liquid crystal formation are two important mechanisms by which detergents can effectively remove soil from substrates. Emulsification involves the breaking of a large oily mass into smaller droplets that can remain suspended for long enough in the cleaning medium to be washed away during rinsing. This process is accelerated in the presence of amphiphilic compounds in the soil, such as fatty acids or fatty alcohols, which can interact with detergents to produce spontaneous emulsification of the soil [120,138,139].

Oily soils containing amphiphilic species, such as fatty acids or fatty alcohols, can also be removed from substrates as a result of the formation of liquid crystal or mesomorphic phases between the amphiphile and a detergent. The liquid crystals are then broken up by subsequent osmotic penetration by water [140–142].

Removal of solid soils by mesophase formation can be accelerated by increasing the temperature. This has been reported for stearyl alcohol [143] and for lauric, palmitic, and stearic acids [128, 129] and is likely due at least in part to the increased penetration of the soils at higher temperatures [128,129,143].

Removal of solid soils by penetration without liquid crystal formation has been reported for tripalmitin, octadecane, and tristearin [143–145]. In these cases penetration of detergents occurred at crack and dislocation sites of soils.

V. ASSESSMENT OF CLEANING EFFICACY OF SHAMPOOS

A. Cleaning of Sebum

The most common soil found on human hair is sebum, a natural oily substance secreted onto the scalp by the sebaceous glands [146,147]. This material, which is a mixture of lipid components (Table 10.15), is distributed more or less uniformly over the hair surface as a result of contact with sebum-filled follicles by

TABLE 10.15 Average Sebum Composition in Adults [115]

Ingredient	Percent of total
Cholesterol	8.65
Free fatty acids	23.39
Triglycerides	32.71
Wax and cholesterol esters	19.53
Squalene	10.31
Paraffins	5.42

hair fibers [148], followed by mechanical actions such as combing, brushing, and rubbing against pillows.

Sebum, when not present in excess, lubricates hair, giving it a smooth and moisturized feel. However, too much deposited sebum causes the hair to become limp and clumped together. Under such conditions, the hair is perceived by panelists as dirty, greasy, and dull. In addition, because sebum is sticky, it tends to bind airborne particles and other materials with which it comes into contact [115,149,150], thus increasing soiling.

Most lipids found on the hair surface come from sebum. Hair also contains internal lipids, which are partly extractable [2,3]; much of this extractable material also appears to originate from the sebaceous glands. Robbins [2,3] has reported that the total extractable lipid can be as much as 9% of the total weight of hair that has not been shampooed for a week. The external and internal lipids are divided roughly equally among this extractable material.

During the relatively short period of time required for shampooing, detergents do not penetrate the hair fiber to any great extent. Shampoos, therefore, largely clean only surface lipid. The internal lipids left behind, however, do not contribute appreciably to consumer perceptions such as soiling, dulling, and feel of hair. Robbins [2,3], for example, found that there is no difference in the quantity of internal lipid extracted from oily or dry hair indicating that only surface lipids were responsible for the oily state of the hair.

An examination of the composition and physical state of sebum suggests that several cleaning mechanisms can operate during its removal from hair. Since sebum is completely molten at body temperature [122], it can be effectively removed by the roll-back mechanism. Also, the presence of approximately 25% free fatty acids in sebum indicates, as discussed in Section IV.C.3, that it is subject to removal by emulsification and mesophase formation. Finally, because the concentration of detergents during shampooing is well above their critical micelle concentrations, sebum can also be cleaned from hair by solubilization.

A number of studies have concluded that anionic surfactants are very effective at cleaning sebum at normal shampoo concentrations [2,3,151–155]. Shaw [152], for example, on the basis of SEM results, concluded that almost complete removal of surface lipid could be effected by anionic surfactants in a single application. Experiments involving extraction of wool swatches and hair clippings led Robbins [2] to reach the same conclusion for two surfactant applications.

The work done by Thompson [153] has shown that sodium laureth-2 sulfate (SLES-2) is superior to ammonium lauryl sulfate (ALS) in cleaning sebum, results that are consistent with those of Clarke and co-workers [152,154]. One reason for this finding is that SLES-2 has a lower CMC and a larger micellar aggregation number than ALS under the same conditions [155,156]. Thus, at a given concentration above the CMC, a solution of SLES-2 is likely to solubilize more sebum than ALS simply because more of its molecules are involved in micelle formation

and it contains larger micelles having increased capacity for solubilizing nonpolar materials.

It should be noted that the results reported above were conducted, for the most part, on virgin hair having a hydrophobic surface. Chemically treated (permed, bleached, straightened, etc.) hair, however, has a more hydrophilic surface than virgin hair, resulting in a lower affinity for sebum and an increased ease of removal for these types of hydrophobic deposits. This reduction in sebum affinity is consistent with the increased dryness and need for conditioning reported for chemically treated and damaged hair.

B. Cleaning of Quaternium Compounds from Conditioner-Treated Hair

As discussed in Section II.B.1, the most commonly used conditioning agents are long-chain quaternium compounds or quats. Two of the most widely used quats are cetyltrimonium chloride (CTAC) and stearyltrimonium chloride (SAC).

Removal of quats such as SAC and CTAC from hair can be expected to be more difficult than the removal of sebum. One reason for this is that the positively charged quats tend to deposit onto hair as a film having a strong electrostatic attraction for the negatively charged fiber surface. Because of the solid nature of these soils, the roll-back mechanism fails to apply, while the positive charge on the quats interferes with the cleaning mechanism discussed in Section IV.B: the mutual repulsion between solid soil and substrate resulting from adsorption of anionic surfactant onto the two surfaces.

Solubilization by anionic surfactants is another possible mechanism for cleaning quats. However, Reich and co-workers [157,158] found that solubilization of CTAC and SAC by lauryl and laureth sulfates (1 to 5 EO) was ineffective owing to formation of surfactant–quat complexes that were insoluble in ALS or SLES and, thus, difficult to remove from hair. In this case, reducing the carbon chain length of the quat to 12 or the chain length on the anionic surfactant to 10 resulted in more soluble complexes and more effective removal of the cationic soil.

C. Cleaning of Cationic Polymers

As discussed in Section II.B.3, Polyquaternium-10 and Polyquaternium-7 (Merquat 550) are two of the most important polymers found in conditioning products.

Polyquaternium-10, also known as Polymer-JR, has a positive charge density of 670 (residue weight per unit of charge) [46,159] and is available with a molecular weight range from 250,000 to almost 1,000,000. Polyquaternium-7, also known as Merquat 550, has a reported positive charge density of 197 [47], which is more than three times the density of Polymer-JR, and a molecular weight of about 500,000.

Many studies on the binding of Polyquaternium-10 to hair have been published utilizing a variety of techniques including radiotracer methods, ESCA, and streaming potential measurements [51,159–161]. It has been shown that Polyquaternium-10 is quite substantive to hair, resisting complete removal by SLS even after 30 minutes of exposure to this detergent.

In radiotracer experiments conducted in the authors' laboratories, deposition of Polymer-JR was found to be almost 2.3 times greater for bleached hair than for virgin hair, indicating a greater number of negative binding sites on the former (Table 10.16).

Similar results were found in experiments run in the authors' laboratories utilizing radiolabeled Polyquaternium-10 (Table 10.17). Under conditions modeling actual hair washing (mechanical rubbing, short treatment times of one minute followed by rinsing), only 43% of bound Polyquaternium-10 could be removed in a single washing with SLS. The removal was increased to 75% for cleaning of Polymer-LR, a polymer with a similar structure to Polyquaternium-10 (JR), but a lower cationic charge density.

Fewer adsorption studies have been published for Polyquaternium-7. These include an ESCA study on hair [113] and a study on adsorption of Polyquaternium-7 from different surfactant solutions [46]. From the experiments conducted in the authors' laboratories (Table 10.16), deposition of Merquat 550 from solution was found to be somewhat lower, although this polymer has a higher reported charge density than Polymer-JR and was at a slightly higher concentration in the test solutions. However, the percent removal from wool was found to be similar for the two polymers. The reason that Merquat 550 is not harder to remove from wool than Polymer-JR remains unclear, despite its higher charge density. It may be due to steric reasons or may be related to the findings of Goddard and Harris [113], who reported that treating hair fibers with equal concentrations of Polyquaternium-10

TABLE 10.16 Deposition of Radiolabeled Polymer-JR 400 on Hair^a

Substrate	mg JR bound/g hair ^b
Virgin hair	0.424
Bleached hair	0.962

^aTest procedure: 0.67 g of 1.76% [¹⁴C]Polymer-JR in water was applied to 2 g tresses and rubbed into the hair for 1 minute. Tresses were then rinsed in a beaker of tap water for 45 seconds, followed by rinsing in a second beaker for 15 seconds, and a final rinse under 38°C running tap water for 1 minute. Portions of hair taken from the tress were then dissolved in 2 M NaOH at 80°C, oxidized with H₂O₂, then mixed with Aquasol-2 LSC cocktail and perchloric acid and counted.

^bEach number represents an average of 5 replicates.

TABLE 10.17 Deposition and Cleaning of Polycationic Conditioners^a

Treatment	mg polymer bound/g wool ^b	Cleaning (%)
1.76% Polymer-JR	5.77	—
1.76% Polymer-JR/5% SLS	3.27	43
1.5% Polymer-LR	4.63	—
1.5% Polymer-LR/5% SLS	1.16	75
2.5% Merquat 550	4.78	—
2.5% Merquat 550/5% SLS	2.81	41

^aTest procedure: 0.15 ml of [¹⁴C] polymer solution in water was rubbed into 0.15 g wool swatch for 1 minute, followed by rinsing in a beaker of tap water for 45 seconds, another rinse in a second beaker for 15 seconds, and a final rinse under 30°C running tap water for 1 minute. The same procedure was followed with SLS. Following this, swatches were dissolved in 2 M NaOH at 80°C, then mixed with Aquasol-2 LSC cocktail and perchloric acid and counted.

^bEach number represents an average of 5 replicates.

and Polyquaternium-7 resulted in 25% surface coverage by the former material and only 10% coverage by the latter.

Deposition of Polyquaternium-7 and Polyquaternium-10 from anionic shampoos has been reported to be greatly decreased as a result of the formation of negatively charged polymer/surfactant complexes that are repulsed by negatively charged keratin surfaces [152,157]. As was stated earlier, however, these association complexes are still resistant to removal from hair [51].

D. Cleaning of Fixative Residues

Neutral or negatively charged polymeric resins are commonly employed to provide styling benefits in products such as mousses, gels, hairsprays, and setting lotions. Typical examples in use today are the copolymer of vinyl acetate and crotonic acid, the copolymer of polyvinyl pyrrolidone and vinyl acetate (PVP/VA), the ethyl ester of the copolymer of polyvinyl methyl ether and maleic anhydride (PVM/MA), and the copolymer of octylacrylamide/acrylates/butylaminoethyl methacrylate (Amphomer).

Very few studies have been reported on the cleaning of hairspray resins from hair. In general, these resins are expected to be removed easily from hair due to their noncationic nature. This is consistent with a study by Sendelbach and co-workers [162] who reported 80 to 90% removal of different neutral or neutralized fixatives using a novel gravimetric study. Similar results were found in an experiment in the authors' laboratories employing a radiolabeled ethyl ester of PVM/MA. In this experiment it was found that 89% of the resin was removed from wool swatches with a single washing with 10% ALS.

The above experiments cover a limited selection of hairspray resins. More work needs to be done, therefore, to gain a more complete picture of fixative cleaning from hair, especially for polymers having differing degrees of neutralization.

E. Cleaning of Dimethicone Residues

Dimethicone is the major conditioning agent used in two-in-one shampoos. As with fixative resins, little research has been done on the ease of removal of this material.

Rushton *et al.* [163] have studied the buildup and cleaning of dimethicone using ESCA and atomic absorption measurements. They observed a roughly 35% increase in dimethicone deposition on virgin hair after five washings with a commercial two-in-one shampoo compared to a single wash. No further deposition was observed, however, between 5 and 60 washes. They also found that a single wash with commercial shampoos removed more than 90% of deposited dimethicone. These latter experiments, however, were performed on solvent extracts of treated hair; no evidence was presented to show that all of the deposited dimethicone could be recovered in the solvent extract. More work is needed to determine unequivocally the ease of cleaning of dimethicone deposits.

VI. IMPORTANT ATTRIBUTES OF SHAMPOOS AND CONDITIONERS

A. Viscosity and Spreadability

Spreadability is an important product attribute that is related to viscosity and consistency of a formulation. The desired viscosity for a shampoo is generally between 2000 and 5000 cP: high enough for the product to be held in the palm without dripping but not too high to be difficult to spread over the hair. Conditioners, in general, have a higher viscosity than shampoos, of the order of 3,000 to 12,000 cP. A number of additives including alkanolamides, salts, and quaternary polymers can be used to control the consistency of shampoos and conditioners as discussed in Sections II.A.2 and II.C.1.

B. Lather and Foam

Although not an indication of cleaning efficiency, the ability of a shampoo to provide a rich, copious lather is one of the first performance evaluations made by a consumer. A formulator should be aware that a consumer is likely to perceive a shampoo's lathering potential to reflect its efficacy. With this stated, there are multiple facts of the lathering attribute to consider, such as the speed with which lather is generated, the volume, the quality (i.e., loose or creamy), and the stability of the lather on the hair.

Several methods for generating foam have been reported including the use of kitchen blenders [20,164], shaking or rotation [165,166], by dropping from a height into a flask (Ross–Miles) [167], and by bubbling inert gas into the solution [168].

Hart and DeGeorge [21] employed a kitchen mixer to create lathers and measured the rate of foam drainage. They distinguished foam from lather, indicating that lather is a particular type of foam comprised of small, densely packed bubbles and is generated during shampooing and other processes. They also found that sebum significantly lowered lather quality and stability. This explains why a shampoo at the second application generally lathers better than during the first application.

Domingo Campos and Druguet Tantina [22] compared six methods of measuring foam and concluded that the Hart–DeGeorge method [21] and the Moldovanyi–Hungerbuhler method [168] correlate better with actual in-salon testing than the other four methods. They also concluded that the test should be carried out at a high concentration of about 60 g/l and preferably with the incorporation of a soil.

Robbins suggested that the rate of lather generation and the feel of the foam are two other important elements of shampoo lather. Methods for evaluating these two elements have not yet been well developed [3].

C. Ease of Rinsing

Following lather generation, it is important for a shampoo to be easily rinsed out of the hair. The ease of rinsing of a shampoo is affected by lather consistency, adsorption of surfactant to the hair, water conditions, such as temperature, hardness, and rinsing rate, and the quantity of hair [2]. A good shampoo formula should not contain ingredients that form precipitates in hard water, nor should it leave excessive residue on the hair surface.

D. Mildness

Mildness is an important concern for any type of shampoo and is especially crucial for baby shampoos due to the fact that the product could easily come into contact with skin, scalp, eyes, lips, and nose during the shampooing and rinsing processes. Surfactants and sensitizing agents used in personal care products are the main contributors of irritation.

A variety of test procedures exist for determining the relative mildness of personal cleaning products on human skin. The overall categories for the methods include patch testing, exaggerated use test, consumer use tests, and flex wash test [169–174].

VII. EVALUATING COSMETIC PROPERTIES OF SHAMPOOS AND CONDITIONERS

As described earlier, conditioning is a broad term for several desirable properties a conditioner can offer, including ease of wet and dry combing, shine, softness, manageability, and flyaway reduction. The assessment of these desirable conditioner properties is discussed in the following sections.

A. Ease of Combing

Ease of combing is, of course, one of the main benefits imparted to hair by a conditioner or conditioning shampoo. As such, the measured decrease in combing forces is frequently used to evaluate the effectiveness of a conditioning product.

Quantitative combing measurements can be performed using a Diastron or Instron tensile tester on both dry and wet fibers [175–178]. In this procedure, a comb is passed through a hair tress and combing force is recorded as a function of distance. In a typical combing curve, a sudden increase in combing force is generally observed at the fiber ends (end-peak force) as a result of entanglement of fiber tips. Kamath and Weigmann [179] have reported a double-comb method to prealign hair tresses that was claimed to eliminate the entanglement of fiber ends, and as a result produce a more reliable and consistent end-peak force.

A different technique, called spatially resolved combing analysis, was developed by Jachowicz and Helioff [180] to study the conditioning effects and substantivity of Polyquaternium-11 on different types of hairs. They found that bleaching results in a several-fold increase in combing forces compared to untreated hair. Subsequent application of a polymer solution was found to decrease friction against the hair surface and reduce combing forces.

B. Luster or Shine

The luster of hair is another attribute that is very important to consumers. Perhaps in part because of advertising messages, consumers tend to associate shine or luster with hair that is healthy and in good condition.

There are a number of factors that can affect the shine of hair. Shampoos and other hair care products that leave dulling deposits on the hair surface can reduce shine. Luster can also be lost as a result of abrasion, bleaching, grooming, or other stresses that damage and roughen the hair surface. Conditioning agents that reduce chipping and uplifting at scale edges or a shampoo that removes dulling deposits from hair will leave hair in a shinier state.

Hair luster has been evaluated subjectively and instrumentally. Subjective tests can be done on tresses or human volunteers. A number of instrumental methods for measuring hair shine have been reported [181–187]. Among these, light scattering has been used most extensively. Reich and Robbins [181] used a goniophotometer

to measure hair shine quantitatively and found that it is a sensitive means of following changes to the hair surface including deposition (soiling and buildup), particle removal (cleaning), and even interactions on the fiber surface.

A quantitative measure of luster can be calculated from a light scattering curve (Figure 10.5) by the following relationship [181]:

$$L = S/DW_{(1/2)} \tag{3}$$

where L = luster or shine, D = integrated diffuse reflectance, S = integrated specular reflectance, and $W_{(1/2)}$ = width of the specular peak at half its height.

The above equation was found to correlate well with panelists' subjective ranking of hair tresses. Note that the equation cannot be generally applied, since in cases where D equals zero the expression goes to infinity. It is convenient to apply this equation to hair, however, since diffuse scattering from scale edges ensures that D will not have a zero value.

C. Body or Volume

From the consumer's standpoint, body is associated with fullness, volume, springiness, and bounce. Clarke *et al.* [188] stated that the visual impact of voluminous hair moving in a controlled manner is a universal description of hair with body. Another definition of hair body given by Hough *et al.* [189] is "a measure of a hair mass's resistance to and recovery from externally induced deformation."

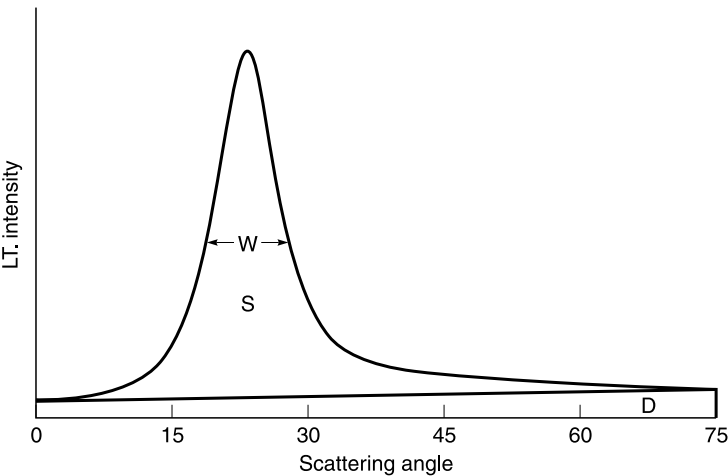


FIG. 10.5 Typical light scattering curve for a virgin oriental hair.

The effects of shampoos and conditioners on hair body depend on the ingredients and the type of hair. A cleaning shampoo can provide body by removing soils or styling residues that weigh down the hair. Alternatively, shampoos and conditioners can deposit materials on the hair surface that can depress hair volume. Straight fine hair is more sensitive to these effects than is curly coarse hair.

A number of instrumental methods have been reported for evaluating variables associated with hair body [189–193]. These methods measure changes in fiber friction, stiffness, curvature, diameter, weight, cohesion, and length. Treatments that increase the hair's curvature or diameter, increase the friction forces between fibers, or make the hair stiffer will increase body. Those that increase the cohesion between fibers or weigh them down will decrease hair body.

D. Surface Conditioning and Wettability

Wettability determinations provide important information on surface properties of different materials. A healthy hair fiber, for example, is covered by a hydrophobic lipid layer that lowers the energy of the hair surface and prevents the fiber from being wetted by liquids with a high surface tension, such as water. The surface energy of a clean hair fiber, therefore, as reflected in its wettability, provides information on the degree to which the surface layer is intact and the hair is undamaged. Wettability measurements also provide information on the substantivity of conditioning agents, and the uniformity of deposited films.

The wettability of hair surfaces can be determined using the Wilhelmy technique, in which the force exerted by the wetting liquid (usually water) on an individual fiber is scanned along the fiber length [194,195]. The wetting force (F_w) or contact angle (θ) is then given by the Wilhelmy equation:

$$\cos \theta = F_w / l\gamma \quad (4)$$

where θ = solid–liquid contact angle, F_w = wetting force at any submersion position, l = wetted circumference of the fiber, and γ = surface tension of the liquid, usually water.

In general, the advancing contact angle for undamaged hair is greater than 90° , reflecting a hydrophobic surface [194] and a low value of F_w in the above equation. Weathering and chemical treatments typically make hair more hydrophilic, resulting in a decrease in the contact angle and an increase in wetting force.

E. Hair Strength

Chemical treatments, UV radiation, chlorine compounds from swimming pools, and oxidative pollutant compounds are all known to damage hair and reduce its strength [78–83].

The mechanical strength of a hair is determined by measuring its tensile properties using a Diastron or Instron tensile tester. The slope of the post-yield and the breaking force obtained from a typical stress–strain curve have been found to relate to the loss of mechanical strength of the hair and to the percent reduction of disulfide bonds [79,82,196].

F. Flyaway Reduction

The phenomenon of flyaway is a result of charge repulsion between hair fibers, which makes hair hard to comb or to keep in place. This problem occurs when hair is combed or brushed, particularly at low humidity. The generation of static charges is due to an unequal transfer of charges across the interface between materials in contact.

Lunn and Evans [197] found that the density of charge is greatest near the tips of fibers, which corresponded to the highest combing force on the hair and that the forces acting between fibers and comb are directly related to the mutual area of contact and determine the magnitude of charging. This means that the magnitude of friction is directly involved in electrostatic charging. They concluded that quaternary ammonium compounds reduced static charge by reducing combing forces and that the half-life of charge mobility is dependent upon the concentration of quats. Jachowicz *et al.* [27] suggested that an increase of surface conductivity by long-chain alkyl quaternary ammonium salts is another mechanism by which these materials reduce static charge.

The measurement and control of electrostatic charge has been studied more extensively on textile materials than on hair fibers. Methods reported in the literature for static charge measurements include resistivity measurements, Faraday cage [197], dielectric losses, and TSC (thermally stimulated current) spectroscopy [198].

G. Manageability

Manageability, an important term in hair cosmetics, is a complicated attribute and is difficult to evaluate with a single parameter. The assessment of hair manageability is further complicated by other variables, such as the type of hair, humidity, or hairstyle.

Robbins *et al.* [199] defined manageability as the “ease of arranging hair in place and its temporary ability to stay in place” and suggested that hair manageability consists of three critical hair assembly properties: style arrangement manageability (combing or brushing of hair), style retention manageability (style retention during styling process), and flyway manageability (static flyaway).

VIII. DAMAGE TO HAIR FROM SHAMPOOS

Shampoos can damage the hair in different ways. Okumura [200] claimed that damage to the cuticle is a result of fibers rubbing against each other during the lathering stage. The removal of sebum, a natural lubricant for hair, from the fiber surface during shampooing also increases the susceptibility of hair to subsequent surface damage from combing and grooming. Kelly and Robinson [201] suggested that combing, brushing, and towel drying damages hair more than the lathering process. They also found greater cuticle loss from wet combing than from dry combing.

Damage to the interior of the hair fiber can also result from exposure to shampoos. Many studies have indicated that the hair structure is disrupted by surfactants that can slowly dissolve or remove structural proteinaceous materials. The number, percent, and mean area of voids or holes appearing in the endocuticle region after repeated washing and drying have been observed [202,203] using imaging analysis and TEM (transmission electron microscopy).

Sandhu and Robbins [204] found that hair fibers shaken with SLS and ALS solutions lost more protein than in water alone. Marshall and Ley [205] were able to extract protein from cuticle cells after a short 1 minute agitation in 1% SLS.

Recently, there has been increasing evidence that interior lipid material, much of which is structural, can be removed by shampooing [202,206]. The internal lipids removed over time by repeated shampooing are most likely from the inert (β) layers of the cell membrane complex which is the major pathway for entry of surfactants into the fibers.

IX. SAFETY CONCERNS

Very few adverse effects have been reported for shampoos and conditioners, especially when usage instructions are followed.

The potential health risks of personal care products that can occur include skin or eye irritation, ingestion, and inhalation. In general, surfactants used in shampoos do not demonstrate serious oral and ingestion toxicity.

Perfumes, preservatives, and emollients in cosmetic products are reported to be the major sources of adverse effects [207]. The problems that have been reported include temporary hair loss, contact dermatitis, scalp seborrhea, photosensitivity reaction, and mild acneform eruptions and folliculitis [208]. Bergfield attributes these problems either to preservatives or medicated ingredients rather than the active ingredients of hair products.

X. FORMULATION TECHNOLOGY

A. Formulation

The requirements for an effective commercial shampoo and conditioner have been touched on and discussed in some detail in the preceding sections of this chapter.

Essentially a good commercial shampoo formulation:

- Must clean effectively
- Must provide acceptable lather
- Must be stable with respect to phase separation, microorganisms, color, and fragrance
- Must be sufficiently easy to manufacture

Except for cleaning and lather, the above considerations also apply to a commercial conditioner. In the following sections, each of the above requirements is discussed.

B. Formulation Requirements

1. Cleaning

As discussed earlier, shampoos have relatively high surfactant concentrations to ensure high lather and viscosity. For most types of soils, this also ensures adequate cleaning by shampoo detergents, including the two most common types of surfactant, ALS and ALES or SLES (see [Section V](#)).

In many systems, ALS delivers better lather and is easier to thicken than ALES or SLES, while the latter surfactants are milder and clean hydrophobic materials somewhat better, especially in hard water [152–154]. To take advantage of these differences, many formulations employ combinations of the two types of surfactant as their primary surfactant systems.

2. Lather

Generation of adequate lather is one of those product attributes that are crucial for a shampoo to be acceptable to consumers. Rich lathers can generally be attained through use of sufficiently high concentration of a primary, anionic surfactant together with a suitable secondary surfactant.

Common secondary surfactants employed to boost or modify lather include cocamidopropyl betaine, cocamide DEA, cocamide MEA, and cocamidopropylamine oxide. Anionics, such as disodium lauryl and laureth sulfosuccinates are also employed in some products as foam boosters.

Some ingredients in shampoos, notably dimethicone, can depress lather. The presence of these materials must be compensated for, by increasing surfactant concentration, changing the secondary surfactant, or adding additional foam boosters such as cetyl alcohol.

The particular materials chosen depend upon the formulation and its requirements. The effect of a particular foam booster on surfactant structure can vary with the formulation, especially if it is a complex emulsion containing many structure-modifying ingredients. In this case, several different lather modifiers should be investigated to optimize product lather.

3. Viscosity and Rheological Characteristics

As stated earlier, both shampoos and conditioners must have sufficiently high viscosities to remain easily in the hand. In addition, however, the product must also have the correct rheological profile. Thus, it must have good stand-up in the hand, but must be sufficiently shear thinning that it is dispensed easily from the package.

In addition, shampoos and conditioners must spread easily over the hair, must not be stringy, and must not get too thick or too thin with changing temperature.

For simple cleaning shampoos, adequate rheological properties can generally be obtained by the same methods used for lather: sufficiently high primary surfactant plus the same secondary surfactants listed above as lather modifiers.

A particular viscosity level is then attained through addition of salt, usually sodium chloride (Section II.C.2). Salt increases viscosity up to a point, after which addition of more salt reduces viscosity. Generally, shampoo viscosity is adjusted on the rising portion of the salt curve.

For more complex shampoos, including emulsions, a variety of thickeners is available besides salt, including gums, associative thickeners, synthetic polymers, and long-chain alcohols (Section II.C.2). These materials are used to attain a desired viscosity, to stabilize a product, and to attain a desirable rheological profile. Since they affect product structure, they can also affect lather. Viscosity modifiers, therefore, should be chosen to give the best mix of lather and rheological properties.

C. Stability

1. Types of Product Instability

Commercial products should have a shelf life of the order of two years. Over this time period viscosity, color, and fragrance should not change appreciably, and phases should not separate or materials precipitate out of the product.

The products most at risk are emulsions and colored formulations in clear packages. The latter are subject to exposure to radiation from sunlight resulting in possible color fading and also photodegradation of other light-sensitive components of the formula, especially in the fragrance. This type of instability can be handled by removing any nonessential light-sensitive materials and addition of antioxidants and UV blockers (Sections II.C.4 and II.C.5). The last mentioned can be added to the formulation or incorporated in the walls of the package.

Most conditioners and two-in-one shampoos are oil-in-water emulsions that are subject to phase separation of insoluble hydrophobic components. Standard emulsion technology must be employed when phase separation occurs. This can include changing orders of addition, adding energy in the form of increased temperature or higher stirring rates, different mixer configurations, increasing concentrations of stabilizing agent, adding a new or second stabilizing agent, etc.

2. Instability Testing

In general, a formulator cannot wait while a product ages for a year or two to determine its stability. Accelerated aging tests are therefore run, usually at elevated temperatures, to predict shampoo and conditioner stability. There are no standard accelerated aging tests in the hair care industry; each manufacturer has developed its own tests based on research and experience.

For evaluating physical stability, Robbins [3] has suggested running accelerated tests by placing formulations in ovens at 40 and 50°C for periods ranging from three to six months, along with aging at 25°C for one year. Products should also be subjected to one or more freeze–thaw cycles to evaluate stability at low temperatures. Note that elevated temperatures cannot be used to predict physical stability if a phase change occurs at the higher temperature, since one is no longer evaluating the same product. Under such conditions, it is even possible for a product to be unstable at room temperature and stable at higher temperatures.

For sunlight stability, products can be evaluated after exposure in their packages to direct sunlight for various periods of time. Accelerated aging can also be evaluated in instruments such as the Atlas Weatherometer in which products can be subjected to intense radiation at elevated temperatures.

D. Manufacturing Ease

The different components in a formulation and their interactions and compatibility with each other all have an effect on the ease with which a product is manufactured.

Generally, simple cleaning shampoos with no insoluble ingredients are easiest to manufacture: they are simply mixed together in a vessel at room temperature. Even in this case, however, the order of addition may be important. Adjustment of pH should be carried out at the end of the process. If possible, adjustment of viscosity should be the last manufacturing step, since mixing solutions having high viscosity requires greater energy and can lead to excessive aeration.

Adding solid amides to modify lather and viscosity increases manufacturing complexity since heating above the melting point will generally be necessary. Even detergent-soluble solids may require heating in order to dissolve these materials in a reasonable amount of time. When possible, such materials should be predispersed or dissolved in the fragrance.

Conditioners and two-in-one shampoos, which are generally oil-in-water emulsions, are more difficult to manufacture than simple cleaning shampoos. Emulsions require energy to break up properly an oil phase and disperse it in water. This can be accomplished by energetic mixing, often aided by heating. Obtaining sufficiently energetic mixing may require different mixer types and configurations than would be required for a simple solution.

Order of addition is ordinarily important for obtaining the desired emulsion. With certain types of thickeners, this may mean that viscosity rises in the middle of the manufacturing process, making mixing and oil phase dispersion more difficult.

Many stabilizing agents, including some for dimethicone, are insoluble solids. Use of these requires heating above the melting point for both the water and oil phases of the formulation. The higher the melting point of the solid, of course, the higher the manufacturing temperature, and the more time and energy will be required to heat the formula and to cool it down. Choosing a predispersed or low-melting solid will improve manufacturing ease, but may increase formula cost.

Finally, many desirable silicone conditioning agents present handling difficulties. Dimethicone, while liquid, may have a viscosity so high that dispersal in the water phase along with cleaning after manufacture becomes difficult. Similar problems arise with solid silicones and gums. As a result of these difficulties, many manufacturers offer pre-emulsified silicones having low viscosity. As with other predispersed materials, increased manufacturing ease must be balanced against increased cost.

XI. NEW PRODUCTS AND FUTURE TRENDS

A. Increased Use of Natural Materials

The market for natural personal care products has been growing at double-digit rates in the past few years and the trend is expected to continue for many years to come [209]. Natural and nonsynthetically derived ingredients are perceived by many consumers as being milder, safer, and more environmentally friendly.

Natural materials have been gaining popularity in shampoos and conditioners to support a wide variety of claims including conditioning, strengthening, luster, body, antidandruff, color retention, moisturizing, and photo protection.

Many natural materials provide real benefits and may be used either alone or in conjunction with their synthetic counterparts. The benefits from other materials may not be well documented or claims may be based on folklore or on benefits provided to other parts of the body, such as skin, rather than to the hair. These materials may be added to the product as marketing ingredients. As such, their purpose would be to differentiate the product and to capitalize on an ingredient's natural source or its association with health.

Table 10.18 lists some natural ingredients in the patent literature or in use in current hair care products along with their claimed benefits.

B. Increased Need for the Aging Population

The “baby boomers” born between 1943 and 1964 are moving into middle and old age. In 2003 they represented 27.7% of the U.S. population [227]. This group is

TABLE 10.18 Natural Ingredients Found in the Patent Literature or Current Hair Care Products and their Claimed Benefits

Natural ingredient	Claimed benefits
Keratin and derivatives, hydrolyzed protein, collagen protein, silk, and hydrolysate	Strengthening damaged and weathered hair fibers [210–213]
Essential oils and fragrances	Antistress, calming, and aromatherapeutic
Rosemary, sage, echinacea, camomile	Add sheen to hair
Hemp seed oil	Shine and conditioning effects [214]
Zingiber zerumbet extract (awapuhi)	Cleaning and conditioning [215]
Fruit concentrates containing fruit acids, vitamins B3 and B6, fructose, and glucose	Nourish and smooth the hair
Vitamins C and E, ginger root, green tea, rosemary, cranberry fruit, and grapeseed	Antioxidants and antiphotaging [216]
Green tea extract, sage, Indian hemp, and rosemary	Anti-inflammatory, scalp itching or irritation control [217]
Grapefruit, lemongrass, and green tea	Lift sebum and flakes away
Basil, sage, mint extracts	Minimize oil production, add luster
Saw palmetto, lotus, and honey	Slow down hair loss, promote hair growth [218–222]
Chitosan	Improve hair strength and smoothness [223], reduce skin irritation [224], intensify coloration of hair dyes [225]
18-Methyleicosanoic acid (18-MEA)	Restore shine, softness, and silkiness to long hair [226]

more aware of the importance of a healthy life style than the preceding generation at the same age and is willing to pay more for premium products.

This generation is encountering a higher incidence of hair thinning, loss, and graying. Hair products that claim to provide antiaging benefits, including hair loss prevention [218–222,228–234], hair darkening [235,236], hair thickening [237], and graying reduction [219], are becoming more important to this generation.

Procter & Gamble and L’Oreal have been very active in investigating compounds and formulas for promoting hair growth or slowing down hair loss [228–234]. Currently, in this segment of the market leave-on products are dominant.

C. Ethnic Hair Care Market

Hair care products have traditionally been formulated for Caucasian hair. In 2003 African-Americans made up 13% of the U.S. population and accounted for 30%

of hair care sales. The ethnic hair market requires very different styling, coloring, and conditioning products as a result of the very different hair textures and styling habits of African-Americans.

African-American hair is tightly twisted with a large degree of curl. This hair tends to be dry due to the structure of the hair and its curly nature. In addition, some African-Americans like to wear their hair relaxed, a process that causes excessive damage to the hair fiber. Products that provide moisturization, frizz control, breakage reduction, and shine are most desirable for African-Americans.

D. Increased Demand for Specialty Products

Products for special, individual needs have been gaining dramatic acceptance among consumers with specific cosmetic or health concerns. The demand for specialty products is driven by race, age, gender, image, personality, lifestyle, health, well-being, fashion, etc. New specialty shampoos that have been developed and are emerging into the market include volume control [238–241], color protection [242], sun protection [84,243–246], revitalization or repair for damaged hair or split ends [247], frizz and flyaway reduction [248,249], styling control [250–260], etc. Currently, because they provide much greater actives delivery, leave-in products are more likely to provide real added benefits than rinse-off formulations.

E. Nanotechnology

Nanotechnology is becoming a very promising technology in many areas. The use of nanoparticles of ingredients makes it easier to suspend water-insoluble actives in the medium, thus improving product stability and actives delivery. NanoSal, a controlled delivery system based on nanospheres, has been patented as an effective delivery vehicle for a broad range of ingredients and sensory markers onto skin, hair, and hair follicles. A prolonged release rate of active materials has been claimed [261]. This technology is especially valuable for rinse-off products, which have generally a very low amount of deposition compared to leave-on products. The systems can also provide heat-triggered release of active agents and yield a high-impact fragrance burst upon blow-drying of the hair.

L'Oreal has been granted several patents on nanoemulsions based on polymers, anionic polymers, and fatty esters of phosphoric or glycerol [262–268]. They have also patented nanocapsules that protect actives from premature release before reaching the targeted site for cosmetic, dermatological, and pharmaceutical applications [269–272]. Sunscreen formulations containing nanopigments based on metal oxides, like titanium oxide and zinc oxide, for improvement of sun protection factors (SPFs) of skin and hair products have also been extensively covered [273–278]. In addition, the use of ammonium oxide nanoparticles [279,280] in shampoos has been claimed to deliver very good hair retention and styling benefits as well as to harden and straighten hair fibers.

Procter & Gamble [281] has developed very recently a network of nanosized fibers containing chitosan and claimed that this composition would be useful in many areas, including hair care, skin care, oral care, water treatment, and drug delivery.

Up to now, nanotechnology has been applied more for skin care than hair care products. However, based on the similarities of the surface properties between skin and hair, the application of nanotechnology across a wide range of cosmetic products including hair products is expected to grow in the near future.

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