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HAIR PREPARATIONS

The phenomenal growth of the personal care market since the 1940s is a result of socioeconomic changes combined with an increasing focus on personal aesthetics, assisted by affordability of products. The attempt to satisfy the freshly awakened needs of the consumer and the drive for competitive advantages among markets has led to a variety of grooming aids and products; ie, shampoos to cleanse the hair, hair rinses and conditioners to make it soft and combable, hair colorants and permanent waves to impart to hair properties it did not have, and setting preparations and hair sprays to keep hair in the desired style.

Hair products are normally cosmetics and are thus subject to all laws and regulations that control the labeling and claims of all cosmetic products. There are, however, several significant variations to this premise, ie, hair colorants, professional use only products, and products that make drug claims.

0.1. Structure and Composition of Hair

The essential growth structures of hair are follicles which are deeply invaginated in the scalp tissue in the tens of thousands. At the base of each follicle, the cells proliferate. As they stream upward, the complex processes of protein synthesis, structural differentiation, alignment, and keratinization transform their cytoplasm into the tough and resilient material which is known as hair. Hair grows at a rate of about 1 cm per month for a period of 3–5 years, followed by a resting period of 4–6 months, during which the old hair is shed and a new growth begins.

Scalp hair is typically 50–80 μm in diameter and its exterior consists of a layer of flat, imbricated cuticle scales pointing outward from root to tip. This arrangement of cuticle cells permits better mechanical retention of the fiber in the follicle and also serves as a self-cleaning feature. Although the individual scales are thin, ie, 0.5 μm, they are long and overlap each other to form a continuous multilayered shield (3–4 μm) around the fiber. Enveloped by the protective sheath of the cuticle is hair cortex which constitutes the bulk of the fiber. The cortical cells are fibrillar in nature, highly elongated, and oriented along the length of hair. Dispersed throughout the structure of cortex are pigment particles called melanin. Their number, chemical character, and distribution pattern determine the color of hair. In some hairs, centrally located vacuolated medulla cells are also present.

Chemically, hair is a biopolymer composed largely of cystine-cross-linked proteins termed keratins. Two principal protein fractions have been isolated from hair, ie, low and high sulfur proteins. The low sulfur fraction consists of protein of high molecular weight and high degree of molecular organization, ie, α-helical; the protein of the high sulfur group are of low molecular weight and of unknown structural pattern. Electron microscope studies reveal that both proteins participate in a biphase composite, filament-matrix texture which is the dominant structural element of hair cortex. The filaments are composed of low sulfur proteins and the surrounding matrix is made up of high sulfur proteins. The structure and chemical composition of the cuticle differs from that of the cortex, and cuticle cells do not seem to contain any organized low sulfur proteins. The distal zone of each cuticle is heavily cross-linked by cystine; this fact, in conjunction with the multilayered structure, makes the cuticle a formidable barrier to penetration of materials into the interior of the hair.

Although hair of different racial origin differs in shape, degree of waviness (curl), and color, there is very little difference in the underlying chemical composition and physical structure. The rate of reaction with a variety of chemical reagents and most physical properties are similar (1, 2). Differences between hair from different ethnic groups are much smaller than the variation in the properties of hair taken from different individuals within one ethnic group. Compared to Caucasian hair, Negro hair is more oval in the shape of its cross-section, and is much curlier. The tight curls are occasionally associated with unevenness in fiber diameter, resulting in weak spots along the fiber length. These could cause problems during chemical treatments as well as during hot combing. Asian hair tends to be more perfectly round than Caucasian hair and somewhat thicker in diameter, on the average (1). The greater fiber diameter results in a slow uptake of dyes because the ratio of surface area to volume is smaller.

1. Shampoos

One of the largest segments of the hair care market is the shampoo category. With development of mass marketing, the number of shampoos available has reached immense proportions; this has been aided by the availability of synthetic detergents. Synthetic detergents, which have replaced (ca 1993) most soap-based products used in shampoos, allow for greater formulating flexibility and control, and meet new product standards. In the early 1990s a shampoo must not only cleanse and have tolerance to hard water, but it should also be able to provide different performance effects. Through the use of synthetic detergents, new technology, and novel additives, various options in formulating offer consumers a number of alternative shampoo types (see also Detergency; Surfactants).

1.1. Properties

The primary purpose of a shampoo is to clean the hair and scalp. In its cleansing process the typical shampoo must be able to remove the various soils found on the hair and scalp, ie, natural oily exudates and scales; conditioners and setting products that may be applied; and airborne soils that accumulate on the hair and scalp. The shampoo should leave hair soft, lustrous, and in a manageable condition without leaving a harsh, dry, raspy feel. With the use of synthetic detergents there is no problem in providing good cleansing; in fact the development chemist is concerned with product over-cleaning. Thus, a good performing shampoo should not completely remove all the oils while cleaning the hair.

There are a number of factors in formulating an acceptable shampoo product. In addition to cleansing, the shampoo should have good lathering properties. Although it has nothing to do with cleansing, the lather connotes a pleasant consumer experience, allowing easy spreadability of the shampoo during the cleansing process. Lathering of the shampoo should take place in either hard or soft water and the lather should be easily and completely removed from the hair without leaving a residue. Further, an acceptable shampoo should be safe for repeated use, nontoxic and nonirritating, adequately preserved, chemically and physically stable, and not damaging to the eyes; it also should have a pleasant fragrance.

1.2. Product Forms

Shampoos generally consist of an aqueous solution or dispersion of one or more cleansing additives, together with other ingredients to enhance performance and consumer acceptability, ie, foaming enhancers, preservatives, colors, fragrances, and pearling agents in the case of opaque shampoos. Other additives found in shampoo compositions include thickeners, conditioners, antidandruff agents, lime soap dispersants, sequestrants, and buffering agents.

Shampoos have been prepared in various forms, and have included systems that are thick and thin, clear and opaque, pourable liquids, solids, gels, pastes, powders, flakes, and aerosol types. In many cases, shampoos have been prepared and directed for various hair types, eg, normal, dry, damaged, and color treated. Most marketed shampoos (ca 1993) are primarily clear liquid and opaque lotion types; gel and paste forms also are available. Aerosol shampoos are available to the consumer; however, their impact on the market has been limited to the dry shampoo aerosol.

1.2.1. Clear Shampoos

Aqueous solutions of one or more detergents, together with other water-soluble modifying additives, are the usual makeup of clear shampoos. The clarity of the shampoo offers the impression of superior cleansing and better rinsing qualities. In formulating, it is essential that components used in these products have low cloud points to maintain clarity at low temperature storage conditions. This is achieved through the careful selection of cleansing agents, additives, and solubilizers. The viscosity of these products is controlled through adjustment with salt and/or the use of alkanolamides or cellulosic thickeners.

1.2.2. Gel Shampoos

These shampoos are generally versions of the clear product but consist of higher concentrations of the cleansing and thickening agents. They are usually packaged in tube form for dispensing purposes.

1.2.3. Opaque Shampoos

Lotion shampoos are opaque in appearance, offering the consumer a range of rich consistencies. These products are usually formed through suspensions of opacifying agents of the glycol stearate type, which often lead to a pleasing pearlescent appearance. Since clarity is not of concern with these products, less soluble cleansing agents can be used. These shampoos also are prepared with dispersions of oils, silicones, and antidandruff additives for specific hair and scalp treatment effects. Thickening agents are used to increase viscosities of these shampoos in order to maintain the various opacifiers and dispersed agents in suspension.

1.2.4. Paste Shampoos

These shampoos represent thickened versions of opaque shampoos. They have a somewhat firm, cream-like consistency and are packaged in jars and/or tubes. Thickening of these systems is usually accomplished through additions of stearate soaps and electrolytes.

1.2.5. Aerosol Shampoos

These shampoos constitute a very small percentage of the market. They have been available in two versions, ie, liquid foam types and dry spray forms. The liquid foam type, despite its convenience and appealing appearance, did not attain high general use. Factors involved in its low acceptability include not only higher product cost but also serious stability issues with can corrosion.

Aerosol dry shampoos fill an important market for those unable to tolerate wet hair, such as the sick and infirm. These products are based on oil absorbing powders which include talc, starch, and/or clay. They can be sprayed onto hair and then brushed off after absorbing soils from the hair.

1.3. Synthetic Detergents

Examples of shampoo formulations are given in Table 1. The names of the ingredients are those designated by the Cosmetics, Toiletry and Fragrance Association (CTFA).

At one time, soaps were the prime cleansing agents in shampoo products. Synthetic detergents are now (ca 1993) the backbone of most shampoo products, but soap systems are used in a few specialty brands. Soap shampoos provide good lathering and rinsing characteristics except in situations where hard water is available.

Table 1. Formulations of Typical Shampoos

Ingredients	CAS RegistryNumber	Wt %	Function
	Clear shampoo		
sodium lauryl sulfate	[151-21-3]	10.0–20.0	primary surfactant
lauramide DEA	[120-40-1]	4.5	foam booster
methylparaben	[99-76-3]	0.1	preservative
propylparaben	[94-13-3]	0.05	preservative
tetrasodium EDTA	[64-02-8]	0.05	sequesterant
fragrance		0.5	fragrance
D&C Yellow #10	[8004-92-0]	0.004	colorant
FD&C Blue #1	[3844-45-0]	0.0005	colorant
water	[7732-18-5]	to 100.00	diluent
	Opaque, pearlescent shampoo		
sodium lauryl sulfate	[151-21-3]	10.0–20.0	primary surfactant
magnesium aluminum silicate	[1327-43-1]	0.5	suspending agent
glycol stearate	[111-60-4]	3.0	opacifier, pearl agent
cocamide DEA	[61791-31-9]	3.0	foaming viscosity aid
sodium chloride	[7647-14-5]	0.5	viscosity adjuster
methylparaben	[99-76-3]	0.1	preservative
propylparaben	[94-13-3]	0.05	preservative
fragrance		0.5	fragrance
deionized water	[7732-18-5]	to 100.00	diluent

In these cases, poor lathering results and complexing of the soap with the heavy alkali metals of hard water occurs, causing deposition of a dulling film on hair with rinsing. Soap shampoos continue to have followers who find that in their use the hair is left in a conditioned state (3). To capitalize on this effect of soap, some manufacturers of shampoos combine soap with synthetics to obtain the advantages of both cleansing and conditioning.

The use of synthetic detergent has become widespread in a number of product applications. These surfactants are classified according to the electrical properties of their hydrophyllic groups in aqueous solutions; ie, designated as anionic for those negatively charged, nonionic for those with no charge, cationic for those with a positively charged hydrophyll, and amphoteric for those having both positive and negative ionic features.

The anionics are used primarily in shampoo preparations because of their superior foaming and cleansing properties. The nonionics, although good cleansers, have low foaming properties and are not widely used in shampoo formulations. The amphoterics are low foaming detergents and are generally regarded as low cleansers. But they are very mild and often are found in baby-type shampoos. Cationic detergents are poor foamers; however, they are substantive to hair and, as a consequence, are used primarily in systems for hair conditioning purposes.

1.3.1. Anionic Surfactants

In terms of general usage in cosmetic products, the anionics are by far the most widely used and are chiefly found in shampoo systems. They provide the formulator with the basic conditions for preparing these products, ie, foaming, cleansing, and solubility.

1.3.1.1. Primary Alkyl Sulfates. These detergents were first developed in Germany to be less dependent on the use of fats and oils for soap preparation and to have more effective detergents to solve the precipitation problems of soaps. These detergents are prepared from the corresponding fatty alcohols which have been sulfated with either chlorosulfonic acid or sulfuric acid. The fatty alcohols are usually prepared by hydrogenation of fatty acids. The use of the chlorosulfonic acid process continues to be the prime method of preparing alkyl sulfates, although a continuous sulfation process using sulfur trioxide is gaining importance in this detergent's manufacture (4).

The most widely used alkyl sulfate in shampoo preparation is lauryl sulfate. The alkyl component of this sulfate ranges from C-10 to C-18 with a predominance of the C-12 (lauryl) component. By distillation of the fatty alcohol, certain cuts can be obtained which offer the best effects in foaming, cleansing, and rinsing properties for the alkyl sulfate preparation. The range which appears to be most desirable is between C-12 and C-16. Lauryl sulfate detergents are available in various salt forms with the sodium, ammonium, and triethanolamine types being used most frequently in shampoos.

Sodium lauryl sulfate is available in solution, paste, and solid forms. As a solution its activity ranges between 28–30%, and as a paste it is 55% active. With this detergent in a shampoo, inorganic salts can affect viscosity. In addition, the limited solubility of sodium lauryl sulfate requires its judicious use in low cloud point clear shampoo systems.

Ammonium lauryl sulfate [2235-54-3] is available as an approximately 28% active, clear, liquid form. It has greater solubility than the sodium salt and is more likely to be used in formulating clear shampoos. Systems using this detergent show their best stability at pH between 6 and 7. Lower pH would tend to hydrolyze the detergent, eventually releasing ammonia.

Of the lauryl sulfates, the triethanolamine form has the best water solubility. Because of this, it is available from suppliers as a clear solution at an active concentration of 40%. Its main disadvantage is discoloration during storage, ie, yellow to amber, which limits its use in clear shampoo systems.

Shampoos based on lauryl sulfates can range from 6–17% of the active surfactant. However, though they are effective cleansers, the alkyl sulfates tend to be defatting. In an effort to make these shampoos more mild, many shampoos are now based on blends of amphoterics and alkyl sulfates or the less irritating alkyl ether sulfates.

1.3.1.2. Alkyl Ether Sulfates. These surfactants are also found in shampoo applications. They are prepared similarly to alkyl sulfates except that the fatty alcohol is first subjected to ethoxylation; ethoxylation may range from 2 to 3 moles per mole of fatty alcohol. Lauryl alcohol is the typical fatty alcohol reacted. Because of high water solubility, alkyl ether sulfates have low cloud points, making them suited for clear shampoo formulations (5). Viscosities based on the ether sulfates can be easily controlled through addition of inorganic salts such as sodium chloride.

1.3.1.3. Alkyl Sulfosuccinate Half Esters. These detergents are prepared by reaction of maleic anhydride and a primary fatty alcohol, followed by sulfonation with sodium bisulfite. A typical member of this group is disodium lauryl sulfosuccinate [26838-05-1]. Although not known as effective foamers, these surfactants can boost foams and act as stabilizers when used in combination with other anionic surfactants. In combination with alkyl sulfates, they are said to reduce the irritation effects of the latter (6).

1.3.1.4. Fatty Acid–Sarcosine Condensates. These surfactants are prepared by the reaction of fatty acid chlorides with methyl glycine; sodium lauroyl sarcosinate [137-16-6] is an example of this group. They are most effective at pH 5.5–6.0 for foaming activity in soft to moderately hard water. The action of these detergents is greatly reduced under severe hard water conditions. The sarcosinates exhibit compatibility with cationic surfactants and have been suggested for use in formulation of conditioning shampoos (7).

1.3.1.5. Fatty Acid–Peptide Condensates. These protein detergents are reaction products of fatty acid chlorides and hydrolyzed proteins. They are used in shampoos because of their mildness on skin, hair, and to eyes when used alone or in combination with alkyl surfactants (8).

1.3.1.6. Alkyl Monoglyceride Monosulfates. These detergents are among the earliest synthetic surfactants. For example, the sulfated coconut fatty acid monoglyceride in its ammonium salt form offers a shampoo with good foaming and detergency. Shampoos formulated with these monoglycerides are regarded as exceptionally mild.

1.3.1.7. Acyl Isethionates. These are among the oldest of the synthetic detergents and were developed in Germany to overcome problems of hard water. They are prepared by reaction of fatty acid chlorides with a salt of isethionic acid, ie, 2-hydroxyethanesulfonic acid [107-36-8]. These detergents have moderate foaming properties and have seen only limited use in shampoos.

1.3.1.8. Alpha-Olefin Sulfonates. Sulfonation of alpha-olefins yields a mixture of alkene sulfonates, hydroxyalkane sulfonates, and some amount of various disulfonates. These detergents are excellent foamers with good detergency properties. They are unaffected in hard water and their effects are considered superior to the alkyl ether sulfates (9).

1.3.1.9. Alkyl Sulfoacetates. These surfactants are prepared by esterification of sulfoacetic acid or by sulfonation of the alkyl chloroester. They are considered to produce good foaming and are less irritating to the eyes than the alkyl and alkyl ether sulfates (10).

1.3.1.10. Nonionic Detergents. Nonionic surfactants rarely are used as the primary cleansing additives in shampoos. They are generally poor foaming, but have value as additives to modify shampoo properties, eg, as viscosity builders, solubilizers, emulsifiers, and conditioning aids.

1.3.1.11. Alkanolamides. The fatty acid alkanolamides are used widely in shampoo formulations as viscosity and lather builders. They are formed by the condensation of a fatty acid with a primary or secondary alkanolamine. The early amides were compositions of 2:1 alkanolamine to fatty acid. Available technology allows the formation of amides with a 1:1 ratio of these additives. These amides are classified as superamide types. The typical amide used in shampoo preparations usually contains the mono- or diethanolamine adduct, eg, lauric diethanolamide [120-40-1] (see Amides, fatty acid).

1.3.1.12. Amine Oxides. These surfactants are formed by oxidation of tertiary fatty amines, eg, lauryldimethylamine oxide [1643-20-5]. They are used to modify foaming and also may find application as hair conditioning agents in shampoos, ie, acting as antistatic agents to provide manageability (see Amine oxides).

1.3.1.13. Ethoxylated Nonionics. These are the largest group of nonionics. They consist of ethoxylated forms of alkylphenols, fatty alcohols, fatty esters, mono- and diglycerides, etc. Although these surfactants exhibit excellent cleansing properties they have poor foaming, and their application in shampoos has been limited. They can be found as solubilizers and emulsifiers. In some cases, nonionics are combined with certain shampoo surfactants to minimize eye irritation (11).

1.3.2. Amphoteric Detergents

These surfactants, also known as ampholytics, have both cationic and anionic charged groups in their composition. The cationic groups are usually amino or quaternary forms while the anionic sites consist of carboxylates, sulfates, or sulfonates. Amphoterics have compatibility with anionics, nonionics, and cationics. The pH of the surfactant solution determines the charge exhibited by the amphoteric; under alkaline conditions it behaves anionically while in an acidic condition it has a cationic behavior. Most amphoterics are derivatives of imidazoline or betaine. Sodium lauroamphoacetate [68647-44-9] has been recommended for use in non-eye stinging shampoos (12). Combinations of amphoterics with cationics have provided the basis for conditioning shampoos (13).

1.3.3. Cationic Detergents

These find little application in shampoo preparation, primarily because most compositions use anionics as the surfactant of choice. Generally, cationics are not combined with anionics in shampoo formulation because the opposing charge differences of these detergents result in a precipitated complex. Despite their substantivity to hair to provide conditioning, cationics have the deficiency of being severe eye irritants. They generally also have low foaming properties which would limit consumer acceptance of shampoos prepared with them. Cationic surfactants have been recommended for special applications, eg, with amphoterics for a hair conditioning shampoo (11).

1.4. Shampoo Additives

Although the primary function of a shampoo is for cleansing, a number of additives are included in their formulation to enhance and improve properties of the product.

1.4.1. Thickeners

These are used to increase viscosity of shampoos to achieve certain consistency characteristics in the product, from a thickened liquid to gels and pastes. Among the most important materials used for this purpose are the alkanolamides. The chain length of the amide alkyl group and its solubility in the shampoo system are important aspects to be considered in their use for effects on viscosity. In general, as the chain length increases the viscosity response improves. The viscosity increase also is related to the water solubility of the amide; the more water-soluble forms provide a lower viscosity response than the less soluble amides.

Inorganic salts are also used to promote shampoo thickening. These should be used sparingly since an excess may have a deleterious effect on a product's physical stability. Sodium chloride commonly is used in these cases. The additions of sodium stearate and stearic amides can be found in paste shampoos for thickening.

Other thickeners used include derivatives of cellulose such as methylcellulose, hydroxypropyl methylcellulose, and cellulose gum; natural gums such as tragacanth and xanthan (see Cellulose ethers; Gums); the carboxyvinyl polymers; and the poly(vinyl alcohol)s. The magnesium aluminum silicates, glycol stearates, and fatty alcohols in shampoos also can affect viscosity.

1.4.2. Opacifiers

Opaque shampoos are produced by incorporating high melting, wax-like, dispersible materials into their preparation. Some of these materials crystallize in such a fashion that they effect a pearlescence in the product. Opacifying agents found in shampoos include the glycol mono- and diesters, higher fatty alcohols such as cetyl and stearyl forms, stearate soaps, and latex copolymer emulsions.

1.4.3. Conditioners

Conditioning agents are added to shampoos to provide manageability properties to hair, eg, ease of combing, detangling, and reduced static. Although the basic detergent is an important factor in the contribution to hair conditioning, additives can be included in the shampoo composition to minimize any ill-effects the detergents might impart. Materials found in many products for conditioning include lanolin and its derivatives, fatty amine oxides, cationic polymers, cationic guar gums, fatty amines and alcohols, alkanolamides, and quaternary ammonium compounds. Humectants, eg, glycerine, sugar, sorbitol; and oils, eg, fatty glycerides, esters, and silicones, also are used. Other additive products include beer, egg, honey, milk, and herb extracts for conditioning.

1.4.4. Preservatives

Shampoos present an ideal environment for microbial growth which can have a harmful effect on the physical/chemical properties of the shampoo and may pose a health hazard to the consumer. To prevent microbial growth, preservatives are added to shampoos. Among those used are methyl and propyl parabens, DMDM hydantoin, quaternium-15, phenoxyethanol, imidazolidinyl urea, and a mixture of methylchloroisothiazolinone and methylisothiazolinone. The selection of preservative is determined through challenge testing which subjects the product to the worst conditions encountered in manufacture, shelf storage, and use (14).

1.4.5. Other Additives

To provide and maintain the clarity of clear shampoos, the use of either ethyl or isopropyl alcohol may be employed. Perfumes are added to make shampoos more pleasing in terms of odor, while dyes are incorporated to give visual aesthetics to the products. Salts of ethylenediaminetetraacetic acid are found to sequester and prevent formation of insoluble alkaline-earth metal salts.

1.5. Baby Shampoos

These shampoos, specifically marketed for small children, feature a non-eye stinging quality. The majority of the products in this category are based on an amphoteric detergent system; a system combining the use of an imidazoline amphoteric with an ethoxylated nonionic surfactant has been successfully marketed (15, 16). The sulfosuccinates also have been suggested for baby shampoo preparation because of their mildness (17). However, their widespread use for this purpose has been limited.

1.6. Medicated Dandruff Shampoos

Dandruff is a scalp condition characterized by the production of excessive cellular material (18). A number of shampoos have been marketed which are designed to control and alleviate this condition, and many additives have been included in shampoo compositions to classify them as treatment products for dandruff. These additives include antimicrobial additives, eg, quaternary ammonium salts; keratolytic agents, eg, salicyclic acid and sulfur; heavy metals, eg, cadmium sulfide; coal tar; resorcinol; and many others. More recent (ca 1993) systems use selenium sulfide [7488-56-4] or zinc pyrithione [13463-41-7] as active antidandruff shampoo additives. Both of these additives are classified as drugs, but can be found in over-the-counter products. A stronger version, incorporating the use of higher levels of selenium sulfide in a shampoo, is available but requires a prescription for purchase.

1.7. Two-in-One Shampoos

These shampoos are combination cleansing and conditioning imparting products. The conditioning aspect is primarily the ease in wet combing, and a conditioning rinse product is not needed after shampooing. These shampoos were first introduced in the early 1970s. Because they did not perform to the satisfaction of the consumer, these early systems quickly faded from the market. In the late 1980s, new and more effective versions of these products appeared and have a strong presence in the shampoo market (ca 1993). These new products are based on conventional anionic detergents to provide desired physical shampoo properties combined with conditioning additives. An important factor in the re-emergence of two-in-one shampoos was efficient delivery of silicones to hair to make it comb easier and to impart a smooth and soft feel (19). In addition to silicones, quaternaries, cationic guar gums, and polymers are found in more recently introduced two-in-one products.

1.8. Manufacture, Evaluation, and Safety

The manufacture of shampoos is a relatively simple operation requiring a suitable stainless steel kettle with provisions for heating and cooling and equipped with appropriately sized mixers. Although shampoos are easily handled during preparation, precautions should be taken to not aerate the product. Cream shampoos are particularly sensitive to aeration and require more special care in their manufacture.

1.8.1. Evaluation

The performance evaluation of a shampoo is an important aspect in determining its acceptability for consumer use. A number of laboratory tests have been developed for this purpose. Although these give an indication of a product's acceptability, the final evaluation is still found through actual use testing. Laboratory methods are valuable to help assess such factors as foaming, cleansing, rinsing, and wet and dry combing effects in the development of a shampoo. These can be determined under standardized, controlled conditions. More critical evaluations can be made through half-head salon comparisons to competitive products and by panel tests under actual use conditions.

1.8.2. Safety

Shampoos generally do not represent a hazard with regard to skin and eye safety; once used, shampoos are almost immediately rinsed and have little contact time on sensitive areas. To assure this safety, provisions to test the finished product for skin and eye irritation should be made.

2. Hair Conditioners

Hair conditioning can be associated with almost any hair product sold in the marketplace because they all claim some benefit to the hair when used. Thus the term *hair conditioner* can be applied to such products as rinses, hair dressings, setting lotions, and hair sprays. Conditioners are used to provide different effects to the hair; primarily ease of combing, sheen, and soft feel.

2.1. Hair Rinses

These products generally are designed to be used in conjunction with shampoos to provide special benefits to hair, eg, wet and dry combing ease, antistatic effects, shine, manageability, and detangling. In years past, an after-shampoo acid rinse, such as a vinegar and lemon rinse, was considered essential to remove the soap film resulting from available products of that time. With the advent and use of synthetic detergents for shampoo preparation, the effect of soap is no longer a factor. However, shampoos made with synthetic detergents are more efficient cleansers, leaving hair less manageable and more difficult to comb, and hence requiring an after-treatment to alleviate these conditions. Creme rinses containing hair substantive cationic additives have been found useful for this purpose. Their after-shampoo use leaves hair smooth to the touch, easy to comb, and unsnarled. The active ingredients in most creme rinses are quaternary ammonium compounds such as steartrimonium chloride and cetrimonium chloride. Other additives useful in after-rinse hair conditioners include certain fatty amines, amine oxides, and cationic polymers. After-shampoo conditioners also are used to improve the finish of hair with respect to manageability, body, texture, etc. Additives used to obtain these effects include protein additives, silicones, and lanolin and its derivatives. Most rinses are opaque products, although clear versions can be found, and they range in consistency from pourable liquids to thick creams.

2.2. Hairdressings

Products associated with final grooming effects to hair are termed *hairdressings*. They are used to impart not only a holding effect to hair, but also provide an added benefit of giving hair a natural, healthy, lustrous appearance. Hairdressings can be found as liquid or cream emulsions, gels, or as hydroalcoholic preparations. They are usually applied by spreading the product through the hair with the fingers and then combing for an even distribution.

2.2.1. Brilliantines

The primary purpose of brilliantines is to add a level of grooming and to impart sheen attributes to hair. Historically, the main constituent of brilliantines is an oil, usually a mineral oil type, in a rather high concentration; in liquid brilliantines, the concentration of oil can run from 80 to 100% in the formula. Brilliantine action on hair is due to formation of a thin-film coating on the strands of hair fibers; the oil is not absorbed but provides a grooming effect. Higher viscosity mineral oils give better grooming than the lower viscosity oils, but have poorer spreadability properties. To offset this aspect, high viscosity oils are sometimes diluted with other hydrocarbons to enhance their spreading effects.

In certain brilliantine compositions, vegetable and animal oils are used as substitutes for mineral oil. In these systems, because of their potential for rancidity, antioxidants must be included. Other alternatives to mineral oils that have found utility in brilliantines are the polyethylene glycols which come in a variety of solubilities and spreading properties. Use of these materials offers the advantage of chemical stability to rancidity. Other additives found in brilliantines to improve their aesthetics include colorants, fragrance, medicated additives, lanolin, and fatty acid esters.

Solid brilliantines and pomades may be considered heavy-duty type hairdressings. These product types range in consistency from soft textured to wax-like and generally have poor spreading properties when compared to liquid versions. Their main component is petrolatum [8027-32-5] with additions of various waxes to obtain different consistency ranges. Early formulations were prepared with naturally occurring waxes such as spermaceti, beeswax, ceresin wax, and paraffin wax. Synthetic waxes are employed as substitutes for the natural waxes since they can be reproduced with greater uniformity to give more consistent end products.

2.2.2. Alcoholic Hair Tonics

Hairdressing products have been prepared by dilution of various oils with alcohol. This allows for good wetting action of the alcohol and, upon its evaporation, results in a deposition of a uniform thin layer of oil on the hair. Synthetics, which have all but replaced natural oils in formulating these products, provide uniformity of components, chemical stability, compatibility, and a range of emolliencies. Additives found in these products include ethoxylated and propoxylated glycols, ethoxylated ethers, various lanolin derivatives, and ethoxylated and propoxylated diols and triols. Because of the range in solubilities which these additives offer, products can be formulated that are less greasy and oily when compared to those made with mineral or vegetable oils. In addition, to offer more consumer-desired properties, alcoholic hair tonics may contain quaternary conditioners, keratolytic agents, hair setting resins, colorants, and fragrance.

2.2.3. Hairdressing Emulsions

Emulsified hairdressings have been formulated both in liquid and cream forms, and prove to be popular among consumers of hairdressings. They are either water-in-oil or oil-in-water emulsions. Mineral oil is commonly used in water-in-oil hairdressing emulsions. Emulsifiers include magnesium, zinc, or aluminum stearate, beeswax, borax, sorbitan sesquioleate, ethoxylated fatty alcohols, ethoxylated lanolin alcohols, polyglyceryl esters, and acetylated ether esters. Other emulsifiers include absorption bases which allow use of as much as 80% water in preparing these product forms.

Oil-in-water based hairdressings offer good spreading characteristics, have a less greasy feel, and are more easily rinsed than water-in-oil forms. Mineral oil is found in these products, although natural and synthetic oils have been used. The typical oil-in-water emulsifiers are used in preparing these emulsions.

2.2.4. Clear Gel Hairdressings

Clear gel hairdressings come in two forms, ie, microemulsions or setting gels. Microemulsions are systems containing mineral oil which can be blended with emollients, conditioning additives, lanolins, and protein compounds. The formation of these gels is achieved through use of high concentrations, ie, 10–40%, of ethoxylated emulsifiers based on fatty alcohols, lanolin alcohols, sucrose fatty acid esters, and oleyl ether phosphates. Additives used in these systems should not interfere with the clarity of the product.

Setting gels are formed through use of high molecular weight polymers such as the methylcellulose ethers and carboxyvinyl polymers. With these polymers, gels of soft to firm consistency can be prepared which provide hair holding properties. The gels are usually water or water/alcohol based to which soluble grooming agents such as poly(*N*-vinyl-2-pyrolidinone) [9003-39-8] (PVP) can be added. To help modify the film properties of these products, other additives such as lower molecular weight alcohols, lower alkoxypolyoxyalkylene glycols and diols, glycerin, and ethylene and propylene glycols may be used.

3. Fixatives

Fixatives are liquid products used to achieve a desired hairstyle and to temporarily hold that style in place. These products can be grouped into two classes, ie, *styling products* and *finishing sprays*. Styling products are used primarily on wet hair to make combing easier and to give the hair some tack so that the style remains in place as the hair is dried. Once dried, the products leave a nontacky coating of film-forming polymers which hold the hair in the desired style. Examples of this type of fixative include styling mousses, gels, lotions, and spray gels. Finishing sprays, eg, pump and aerosol hair sprays, are applied to the hair after the style is dried and set. They generally are not used to style the hair but rather to hold the hairstyle more firmly than styling products. Spritzes are sometimes marketed as styling products, but their technology most closely resembles finishing sprays.

The method used to apply and dry a fixative affects the degree of stiffness and hold it imparts to the hairstyle. If applied and then manipulated with a comb, brush, or fingers as the polymer forms its film, the adhesive bonds between the hair are broken, the film coating the hair is broken, and the end result is a soft feel with little set retention. If the fixative is allowed to dry undisturbed, then the result is a firmer feel and better hold.

When formulating a hair fixative, the balance between the two principal benefits, hold and styling ease, must be selected. Hold is characterized by the stiffness of the polymer film and its ability to remain stiff when exposed to high humidity. Styling ease is characterized by the product's ability to decrease surface friction of the hair during the combing, drying, and styling process. These benefits tend to be inversely proportional. If a product delivers a strong hold benefit, it will tend to be less suitable for improving styling ease.

Once the proper balance of hold and styling ease is attained, the products are tested for delivery problems, proper degree of tack when wet and no tack when dry, visible flaking of the polymer after it dries, dullness to the hair, excessively coated, heavy, or stiff-feeling hair, ease of wash out, stability problems, microbiological problems, and, for finishing sprays only, quickness of drying. Laboratory evaluations of hair fixatives are usually performed on human hair tresses. The hair is prepared to a standard length, weight, and density. For styling products, the hair is shampooed and rinsed with the excess water squeezed out. The product is applied at a standard amount and the hair combed to evaluate comb drag. The hair is rolled into a standard curl formation and allowed to dry and set. Comparisons are made to a control for stiffness, combing ease, curl resiliency after combing, flaking, and stickiness upon contact with moisture. Additionally, treated curls are evaluated for their ability to maintain a tight curl formation under various humidities.

Finishing sprays and spritzes are sprayed on clean, dry hair and tested for drying time, stiffness, combing ease, flaking after combing and stickiness upon contact with moisture. Additionally, hair holding properties are evaluated by measurements of the curl retention at various humidities. Standardized water-set curls are sprayed with standard amounts of product under controlled circumstances. They are then dried, placed into various humidity levels, and the curl fall monitored at various time periods.

Test salons are often used to evaluate hair fixatives. Half-head studies are performed, with the test product applied to one side of the head and a control product to the other in realistic use amounts. Similar properties as described in laboratory tests are measured. Finished products are often sent to testers' homes where they have an opportunity to evaluate the products in real use situations for extended periods.

Table 2. Fixative Styling Product Formulas

Component	CAS RegistryNumber	Wt %	Function
	Styling gel, firm hold		
deionized water	[7732-18-5]	92.40	solvent
carbomer 940	[9007-17-4]	0.50	gelling agent
PVP/VA (65/35) copolymer	[25086-89-9][a]	2.00	holding polymer
PVP (K-90)	[9003-39-8]	1.50	holding polymer
triethanolamine	[102-71-6]	0.50	neutralizing agent
polyquaternium-11 (20%)		1.00	styling ease
laureth-23	[9002-92-0]	1.00	solubilizer
propylene glycol	[57-55-6]	0.50	solubilizer
disodium EDTA	[139-33-3]	0.05	chelating agent
fragrance		0.20	fragrance
methylparaben	[99-76-3]	0.15	preservative
diazolidinyl urea	[78491-02-8]	0.15	preservative
propylparaben	[94-13-3]	0.05	preservative
	Styling mousse, firm hold		
deionized water	[7732-18-5]	84.35	solvent
polyquaternium-11 (20%)		6.00	styling ease
polyquaternium-4		0.50	holding polymer
isosteareth-10	[52292-17-7]	0.20	foam stabilizer
octoxynol-9	[42173-90-0]	0.30	foam stabilizer
dimethicone copolyol	[64365-23-7]	0.20	styling ease
fragrance		0.15	fragrance
DMDM hydantoin	[6440-58-0]	0.20	preservative
methylparaben	[99-76-3]	0.10	preservative
isobutane/propane blend	[75-28-5], [74-98-6]	8.00	propellants
	Styling spray		
deionized water	[7732-18-5]	57.10	solvent
SD alcohol 40[b]	[64-17-5]	40.00	solvent
PVP/VA (35/65) copolymer	[25086-89-9][a]	2.00	holding polymer
polyquaternium-16		0.50	styling ease
dimethicone copolyol	[64365-23-7]	0.20	styling ease
fragrance		0.20	fragrance

[a] PVP/VA copolymer.
[b] 190°proof = 95%.

3.1. Styling Products

Table 2 lists typical styling product formulations. Styling products use similar types of ingredients to provide their primary benefits, but differ in their physical form, ie, styling gels use thickening ingredients to increase viscosity, styling mousses use propellants and surfactants to create foams, and styling sprays often use alcohol to improve spraying and solubilize water-resistant holding polymers.

3.2. Ingredients

3.2.1. Holding Polymers

The setting or holding ingredient in styling products is the film-forming polymer. Its main functions are to hold the hair in a styled configuration and to stiffen the hair, which increases body and fullness. The dried polymer film should be clear, easy to remove by shampooing, tack-free, and not create visible flakes with combing. The polymer should be completely soluble in the product and show good stability under varying temperature conditions. Amounts of total polymer vary from product to product depending on the performance desired; levels can be found from 1 to 7% with the majority formulated from 3–4%.

Polyvinylpyrrolidinone (PVP), introduced in the early 1950s, was the first synthetic polymer to be used in styling products. It is soluble in both alcohol and water and exhibits excellent film forming properties. It is available in various molecular weights from 10,000–360,000, with the higher weights forming stiffer, more humidity-resistant films. Its principal negative is its hygroscopic nature. It becomes sticky and loses hold under humid conditions. Despite this, it is used widely in a variety of products.

Polyvinylpyrrolidinone/vinyl acetate copolymer (PVP/VA) was developed as an improved, less hygroscopic version of PVP. The monomer ratios control the stiffness and the resistance to humidity; however, too high a vinyl acetate monomer content requires another solvent in addition to water to completely solubilize it.

Polyquaternium-11 is the copolymer of *N*-vinylpyrrolidinone and dimethyl-aminoethyl methacylate quaternized with dimethylsulfate (20). It is used widely but provides little hold to the hair. Its primary advantage is its ability to improve the ease of wet combing and control static while giving a light set hold.

Polyquaternium-4 is the copolymer of hydroxyethylcellulose and diallydimethyl ammonium chloride. It provides a firmer hold than polyquaternium-11 and has better humidity resistance.

3.2.1.1. Natural Gums. These were used in early styling products, formerly called wave sets. Natural gums generally make hazy solutions and the dried film tends to flake. For these reasons they are rarely used. Some of these gums, eg, tragacanth and alginates, can create humidity-resistant films and have limited use for specific product concepts.

3.2.1.2. Conditioning Agents. These ingredients are added to make combing easier during styling by reducing friction between wet hair and the comb. Wet hair is much weaker than dry hair and can be damaged by the mechanical action of combing or brushing during styling. Conditioning ingredients in widespread use include the aforementioned polyquaternium materials, particularly numbers 6, 7, 10, 11, and 16; quaternary ammonium salts such as cetrimonium chloride; silicone compounds such as dimethicone copolyol and amodimethicone; and natural oils such as jojoba, corn oil, and safflower oil.

3.2.1.3. Solvents. The most widely used solvent is deionized water primarily because it is cheap and readily available. Other solvents include ethanol, propylene glycol or butylene glycol, sorbitol, and ethoxylated nonionic surfactants. There is a trend in styling products toward alcohol-free formulas. This may have consumer appeal, but limits the formulator to using water-soluble polymers, and requires additional solvents to solubilize the fragrance and higher levels of preservatives.

3.2.1.4. Gelling Agents. These are used to build viscosity in styling gels. Desired properties include clarity, processing ease, and a plastic, shear-thinning rheology. Carbomer 940 is the most common thickening agent for styling gels and best provides these properties. Carbomers are high molecular weight polyacrylic acids. When dissolved in water at their natural pH of about 3, the polymer only slightly increases viscosity. When neutralized with a base, eg, triethanolamine, triisopropanolamine, etc, negative charges on the carboxylic groups mutually repel, causing a spontaneous stretching of the molecule, thus creating a viscous solution (21). Other thickening agents include hydroxyethylcellulose and hydroxypropyl methylcellulose.

3.2.1.5. Foaming Agents / Propellants. These ingredients are necessary in a styling mousse, the French word for foam. Styling mousses were introduced in Europe in the early 1980s and in the United States in 1983, and they are extremely popular.

The foam structure is the result of dispersed, liquefied gas bubbles (surrounded by the mousse concentrate containing the foam agents) suddenly being released from a pressurized system to atmospheric pressure. The propellant rapidly expands to a gas, thus blowing a foam. The stability of this foam depends primarily on the foaming agents selected and the percent of alcohol used in the liquid phase. Ideally, the foam should be stable in the hand for several minutes after dispensing, but break down when sheared to spread easily through the hair.

Many different types of foaming agents are used, but nonionic surfactants are the most common, eg, ethoxylated fatty alcohols, fatty acid alkanolamides, fatty amine oxides, nonylphenol ethoxylates, and octylphenol ethoxylates, to name a few (see Alkylphenols). Anionic surfactants can be used, but with caution, due to potential complexing with cationic polymers commonly used in mousses.

Hydrocarbon propellants, eg, propane, isobutane, butane, are the most commonly used in mousses. These are insoluble in the mousse concentrate; therefore, vigorous shaking of the can before use is required to properly disperse the propellants. Most products use a blend of two or more hydrocarbons. The more volatile the propellant blend, the faster a foam structure is formed and the less dense it is. An exception to this is the use of hydrofluorocarbon 152A [75-37-6] (HFC) which has partial solubility in mousse concentrates and a high volatility. The high volatility creates an immediate foam structure but the partial solubility leads to a creamy, dense foam. HFC is not an ozone depleting propellant as are its cousins the chlorofluorocarbons (CFCs); additionally, it is not considered a volatile organic compound by the states of California and New York due to its low activity in reactions that create ground level ozone.

3.2.1.6. Preservatives. Most products must contain preservatives to ensure that yeasts, molds, and bacteria do not thrive in them. These preservatives include alcohol, methylparaben, propylparaben, DMDM hydantoin, diazolidinyl urea, and imidazolidinyl urea. The parabens have limited solubility in water, eg, 0.25% for methylparaben and 0.05% for propylparaben (22). If these levels are exceeded in the formula, then the addition of solvents is needed to ensure clear, stable products.

3.2.1.7. Miscellaneous. Many other ingredients are used in styling products. Some have function; some are there to support marketing claims. Fragrances play a significant factor in the aesthetics of the product, but can be difficult to incorporate into the products due to being insoluble in water, thus requiring the use of additional solvents. Ultraviolet absorbers such as octyl methoxycinnamate, benzophenone-4, or DEA-methoxycinnamate are often used in styling products. In addition to their uv protection capability, they also can have a stabilizing effect on the viscosity of gels. Chelators, such as disodium EDTA, are used to improve stability of gels and to increase the efficiency of preservative systems. Proteins are film forming polymers and can act to improve the body and fullness of hair if used in levels of 1–4%. Vitamin derivatives, botanical extracts, marine extracts, and other exotic materials may create real benefits, but they rarely are used in high enough levels due to high cost.

3.2.2. Manufacture

The manufacturing of styling products is relatively simple. Generally, a tank with simple agitation is sufficient for low viscosity products, ie, mousse, spray gels, and sculpting lotions. The use of powdered holding polymers and exotic materials can sometimes create manufacturing difficulties. The effect of the manufacturing procedure on the stability and performance of each formula must always be evaluated.

Styling gels are not as easy to manufacture. The gelling materials used are hygroscopic and tend to clump when added to water. This is particularly true of carbomers and can be avoided by using cool water and slowly sifting the carbomer into rapidly agitated water. Additionally, the use of an educator or in-line powder disperser can decrease this clumping problem.

Mousses pose little manufacturing problem, but because they are aerosolized they must be filled with special equipment. The pressure fill technique requires the container to be filled with mousse concentrate, then a valve is crimped on and a vacuum of approximately 2.4 kPa (18 mm Hg) is pulled. The propellants are added through the valve. Another technique, the under-the-cup method, fills the container under pressure with propellant and crimps the valve, all in one step.

3.2.3. Packaging

There are many shapes, sizes, and forms of packaging used for styling products. Gels are usually sold in a low density polyethylene tube or in a bottle with a pump. Spray gels, heat activated sprays, scrunching sprays, etc, are generally in high density polyethylene bottles with pump spray devices. Mousses are generally packaged

Table 3. Fixative Finishing Spray Formulations

Component	CAS RegistryNumber	Wt %	Function
Nonaerosol			
SD alcohol 40[a]	[64-17-5]	89.42	solvent
ethyl ester of PVM/MA copolymer	[50935-57-4]	10.00	holding polymer
aminomethyl propanol	[124-68-5]	0.23	neutralizer
cetearyl octanoate		0.15	plasticizer
fragrance		0.20	fragrance
Nonaerosol[b]			
SD alcohol 40[c]	[64-17-5]	79.95	solvent
octylacrylamide/acrylates/butylaminoethyl methacrylatecopolymer		4.00	holding polymer
aminomethyl propanol	[124-68-5]	0.70	neutralizer
triethyl citrate	[77-93-0]	0.15	plasticizer
fragrance		0.20	fragrance
deionized water	[7732-18-5]	15.00	solvent
Aerosol			
SD alcohol 40[c]	[64-17-5]	74.65	solvent
VA/crotonates/vinyl neodecanoatecopolymer	[55353-21-4]	4.50	holding polymer
aminomethyl propanol	[124-68-5]	0.45	neutralizer
dimethicone copolyol	[64365-23-7]	0.25	plasticizer
fragrance		0.15	fragrance
isobutane/propane	[75-28-5], [74-98-6]	20.00	propellant
Aerosol[b]			
SD alcohol 40[c]	[64-17-5]	55.00	solvent
VA/crotonates/vinyl neodecanoatecopolymer	[55353-21-4]	4.50	holding polymer
aminomethyl propanol	[124-68-5]	0.45	neutralizer
dimethicone copolyol	[64365-23-7]	0.20	plasticizer
fragrance		0.15	fragrance
deionized water	[7732-18-5]	14.70	solvent
dimethyl ether	[115-10-6]	15.00	propellant
isobutane/propane blend	[75-28-5], [74-98-6]	10.00	propellant

[a] 190°proof = 95%.
[b] 80% volatile organic chemicals (VOC).
[c] 200°proof = 100%.

in aluminum cans because they are pressurized and the high water content tends to corrode tin-plated steel aerosol cans.

3.3. Finishing Sprays

Table 3 gives typical aerosol and pump finishing spray formulations.

3.3.1. Ingredients

3.3.1.1. Holding Polymer. The primary setting agent in finishing sprays is the film-forming polymer. Its principal function is to hold hair in a styled configuration for a period of time in all types of weather. It is also important that the polymer is easily removed with shampooing, does not dull the hair, is not sticky in humid weather, and does not flake appreciably with combing. The polymer should be completely soluble in the total system and in aerosols; the polymer's solubility should not be affected by the propellants. The polymer also must be compatible with the other additives in the product because any precipitation over time can lead to dispensing problems by clogging the pump or aerosol valve. The polymer's kinematic viscosity in the selected solvent system has a large impact on the type of spray that results. Polymer concentrations range from 2–7%

in aerosols and up to 7% in pump versions. Generally, the more polymer in the product, the firmer the hold and the coarser the spray due to an increase in solution viscosity.

Vinyl acetate (VA)/crotonates copolymer became available in the late 1950s. It was the first polymer used in fixatives to contain carboxylic acid groups which, depending on neutralization percent, could produce variations in film properties; eg, stiffness, humidity resistance, resiliency, tack, and removability by shampoo. It has largely been replaced in hair sprays by newer polymers.

VA/crotonates/vinyl neodecanoate copolymer is the most used polymer in aerosol hair sprays (ca 1993). Like its precursor above, it has free carboxylic acid groups which can be neutralized to give various film properties. Recommended neutralizing agents include aminomethyl propanol, ammonium hydroxide, and dimethyl stearamine. Recommended percent neutralization is 90%, but products can be found in the 80–110% range.

Ethyl and butyl esters of poly(vinyl methyl ether)/maleic anhydride (PVM/MA) copolymer were introduced in the early 1960s for use in hair sprays. These polymers also have free carboxy acid groups that can be neutralized. Recommended neutralization is 10%, but products can be found in the range of 5–30%, and recommended neutralizers include ammonium hydroxide, aminomethyl propanol, and triisopropanolamine. These were the most widely used polymers in hair sprays before their use decreased dramatically in the early 1990s.

Octylacrylamide/acrylates/butylaminoethyl methacrylate copolymer became available in the late 1960s. It is a very stiff polymer which gives excellent holding properties in hair sprays. This copolymer is carboxylated at regular intervals and also has cationic groups. When the carboxyl groups are neutralized they take on an anionic character. Recommended neutralizing agents for this copolymer are aminomethyl propanol, triisopropanolamine, and triethanolamine (see Alkanolamines). The recommended neutralization level is 95%, but products are known in the range of 85–130%. The use of this copolymer in hair sprays increased dramatically in the 1980s and into the early 1990s.

3.3.1.2. Plasticizers and Other Film-Modifying Additives. The selection of a polymer neutralizer and the level used can greatly affect the properties of the film upon drying. Additionally, glycols, phthalates, and fatty alcohols tend to soften the polymer film, whereas silicone derivatives, lanolin derivatives, various oils, and various fatty esters plasticize the polymers and lessen moisture absorption; polymers can become overplasticized if too much of these are added, causing the film to soften and feel slick. Fragrance also may have an affect on the film and should be considered in the total selection of plasticizers when formulating a finishing spray.

3.3.1.3. Solvent Systems. The principal solvent for finishing sprays is ethanol. Methylene chloride was used as a cosolvent in the past in aerosol hair sprays containing hydrocarbon propellants, but has been banned. Compatibility in the methylene chloride-free products is now ensured through careful selection of polymer and neutralizers. Traditionally, aerosol hair sprays use anhydrous ethanol as the principal solvent while almost all nonaerosol hair sprays contain some water, generally 6–10%; but beginning in the early 1990s the use of water became more prevalent. Water originally was added to lower the cost of the formulas, but with the states of California and New York regulating the total *volatile organic compound (VOC)* content, its use has become a necessity. The addition of water to hair spray formulas poses some problems. The more water added, the longer the product takes to dry and the stickier the polymer film during drying. The most serious problem is that the kinematic viscosity of a polymer solution increases dramatically. Table 4 shows the change in the viscosity of three hair spray polymers at various water levels. In aerosol hair sprays, the incompatibility of water with hydrocarbon propellants is an additional problem. Dimethyl ether can be used in combination with the hydrocarbons because of its good solubility in water.

3.3.1.4. Propellants. Aerosol hair sprays began using chlorofluorocarbons as propellants in 1948. In 1978, these propellants were banned in the United States for use in hair sprays due to the effect they had in depleting stratospheric ozone (23). To replace these, many gases were explored including carbon dioxide and nitrogen, but the hydrocarbons (propane, isobutane, and butane) were found to create the most consistent sprays throughout the can. Additionally, they did not interfere with performance of the hair spray polymers and were compatible

Table 4. Effect of Water on Kinematic Viscosity,[a]

	Water content, %			
Polymer	0	6.8	15.0	22.7
ethyl ester of PVM/MAcopolymer[b]	5.1	7.3	9.9	10.7
VA/crotonates/vinyl neodecanoatecopolymer[c]	3.8	5.1	6.9	8.2
octylacrylamide/acrylates/butylaminoethyl methacrylatecopolymer[c]	7.5	10.9	14.6	18.0

[a] 5.0% active polymer solutions at 25°C.

[b] Neutralized 10% with aminomethyl propanol (AMP).

[c] Neutralized 100% with AMP.

with ethanol and properly neutralized polymers. The principal problem with using hydrocarbons was their flammability. With the advent of VOC content limits, dimethyl ether is used because of its compatibility with water. Another propellant, hydrofluorocarbon 152A, is used in a few products. It is not considered a VOC nor does it deplete stratospheric ozone; therefore, it can be used to create anhydrous hair sprays that comply with initial VOC limits. However, it is quite expensive and in short supply which limits its use (see Aerosols).

3.3.2. Manufacture

Finishing sprays are easily prepared as simple solutions of the polymers, neutralizers, plasticizers, fragrance, etc, in ethanol. If water is in the formulation, it must be added last. The aerosol products are filled by the methods described for styling mousses.

3.3.3. Packaging

Evaluations of finishing sprays must include stability and performance testing in the finished state. With aerosol packages, pitting and corrosion of the can and flaking of the lining are real concerns. Standards of flammability and combustibility must be followed. Flame extension, flashbacks, and flashpoints must be determined for aerosol sprays and the shipping cases must be properly labeled according to U.S. Department of Transportation (DOT) standards. In both pump and aerosol products, spray rates, spray patterns, and particle size distribution have to be optimized. These can be controlled by variations in pump design in nonaerosols and by variations in valves, actuators, and concentrate/propellant ratio in aerosols.

Aerosol finishing sprays generally are packaged in tin-plated steel containers consisting of a dome, body, and base which may or may not be lined for protection against corrosion. For products containing higher water contents, aluminum is generally used for the package. Nonaerosol sprays are typically packaged in high density polyethylene.

3.4. Health and Safety Factors

Finishing spray products generally have high alcohol contents which create a flammability hazard. This hazard is magnified in aerosolized sprays because hydrocarbon propellants used are very flammable. Deliberate inhalation of aerosols poses a potential health hazard to the consumer that could be fatal. Additionally, spraying a high alcohol content finishing spray into the eyes can cause severe irritation. Appropriate warnings must be displayed on the package. Detailed information covering labeling requirements of fixatives in general are published by the FDA (24).

3.5. Environmental Regulation

In 1978, federal regulation banned the use of chlorofluorocarbons in hair sprays. This forced a dramatic change in the technology of aerosol hair sprays, requiring new formulations and new dispensing parts to accommodate hydrocarbon propellants. In the early 1990s, California and New York enacted strict limits on allowable VOC content; VOCs are defined as any compound containing at least one atom of carbon, but no more than 12 atoms, with a vapor pressure of 13.3 Pa (0.1 mm Hg) or more at 20°C. The regulations were enacted due to the role that VOCs play in creating ground level ozone. In 1992, California allowed a maximum of 80% VOC content in finishing sprays, with reduction to 55% maximum VOC content by 1998 (25). In New York the regulations are almost the same, and other states are expected to follow.

The primary VOCs in hair sprays are lower order alcohols and propellants. In nonaerosols, with typical VOC levels of 88–92%, a drop to 80% can be accomplished with total water addition of about 15%, which causes an increase in solution viscosity and a heavier, wetter spray. In aerosols with typical VOC level of 93–98%, a much bigger decrease is needed. The propellant amount is fixed, requiring an even greater percent of the concentrate to be water, about 23%. This in turn causes difficulties in spraying and may require the use of dimethyl ether as a component of the propellant system. Significant discontinuities occur when 55% VOC levels are attempted. Polymer suppliers are working to develop new materials which may be adaptable to these high water content formulas with the overall goal of approaching the performance standards of anhydrous fixative sprays.

4. Coloring Preparations

Hair coloring preparations have been in use since the ancient Egyptians, and recorded recipes exist in many cultures. These followed the traditional application of plant extracts or metallic dyes, both of which still are used. In the latter part of the nineteenth century, synthetic organic compounds were discovered which eventually led to modern hair coloring.

Among the desired properties of a good hair dye, toxicological safety is of primary importance. Coloration should be achievable in 10–30 min at ambient temperature and from a limited dyebath. These requirements mean that only relatively small molecules can penetrate into hair keratin and for this reason oxidative and nitro dyes have received considerable attention. In addition, the dye should impart a natural appearance to the hair under a variety of lighting conditions. It should produce a minimum of scalp staining and be convenient to use. Sunlight fastness must be good, and though fading depends on the type of product, the various components of the dye mixture must fade uniformly. Though hair tends to be nonuniform in diameter, shade, and history of abuse, the color should be fairly uniform or level from root to tip.

Modern hair colorants can be divided into temporary, semipermanent, and permanent systems. These categories are characterized by the durability of the color imparted to the hair, the type of dye employed, and the method of application (see Dyes and dye intermediates).

4.1. Temporary Hair Colorants

Temporary hair colorants give a color that is easily removed from hair. This is done by using large dye molecules that deposit on the surface of the hair without penetrating the cuticle. Dyes used for this class of hair color are shown in Table 5 (see Colorants for food, drugs, cosmetics and medical devices). Products that use these dyes are applied to the hair, usually after shampooing, and left there without any after-treatment. Under normal conditions color that is applied in this way is very fugitive and the dye can be completely removed by one shampoo. The retail products in this category are called temporary rinses. The transitory nature of these dyes provides both an advantage and a disadvantage to consumers. The products can be considered foolproof in that

Table 5. Temporary Dye Colors

FDA Designation	CAS RegistryNumber	CI name	Type
Ext. D&C Violet No. 2	[4430-18-6]	Acid Violet 43	anthraquinone
D&C Red No. 33	[3567-66-6]	Acid Red 33	azo
D&C Brown No. 1	[1320-07-6]	Acid Orange 24	disazo
D&C Green No. 5	[4403-90-1]	Acid Green 25	anthraquinone
Ext. D&C Yellow No. 7	[846-70-8]	Acid Yellow 1	nitro
D&C Red No. 22	[7372-87-1]	Acid Red 87	xanthene
FD&C Blue No. 1	[2650-18-2]	Acid Blue 9	triphenylmethane
FD&C Green No. 3	[2353-45-9]	Food Green 3	triphenylmethane

Table 6. Formulation of Temporary Hair Dye Product

Substance	CAS RegistryNumber	Wt %
dyes		0.500
quaternized amine		0.200
fragrance		0.100
ethoxydiglycol	[111-90-0]	2.000
methylparaben	[99-76-3]	0.100
nonoxynol-6	[27177-01-1]	0.500
water	[7732-18-5]	96.600

the color can be easily removed if the result is not satisfactory. However, there is a limitation in the amount of color that can be applied, and it is not possible to obtain very dark shades. Complexing the anionic dyes with quaternary amines enables more color to be deposited and a composition with these ingredients with benzyl alcohol and a nonionic resin has been patented (26).

Under certain conditions, so-called temporary dyes can be made to last longer than one shampoo. In salons, these dyes may be applied under a bonnet style hair dryer. At the temperature of the hair dryer ($\sim 50^\circ C$), the dyes can diffuse through the outer layers of the cuticle of the hair, and the color will last for many shampoos.

Temporary hair dye products usually are formulated at a neutral or slightly acidic pH. Besides the dyes, the formulations may contain a small amount of a quaternary amine to neutralize the negative charge on the dyes, a fragrance, a small amount of a solvent or surfactant to solubilize the fragrance, and a preservative (Table 6).

4.2. Semipermanent Hair Colorants

The term semipermanent defines hair color products that give a coloration lasting through 5–6 shampoos. This system uses so-called direct dyes which penetrate into the cortex but slowly diffuse out again when the hair is washed. The depth of coverage is limited and no lightening of color can take place. Nitro and anthraquinone dyes are used mainly, and azobenzenes less frequently. The color produced by a particular commercial product may result from the combination of many individual dyes, eg, three yellows, two reds, two violets, and one blue. A blend is necessary to achieve the desired color and to obtain a match between the roots and the more permeable ends. The nitro compounds, mainly nitrophenylenediamines and nitroaminophenols, provide an excellent range of yellow, orange, red, and violet hues but are deficient in blue; to provide blue tones, aminoanthraquinones are included. These are known as disperse dyes because of their insolubility in water. A partial list of semipermanent dyes includes HC Yellow No. 2 [4926-55-0], HC Yellow No. 4 [52551-67-4], Disperse Blue 3 [2475-46-9], Disperse Violet 1 [128-95-0], HC Red No. 1 [2784-89-6], and HC Orange No. 1 [54381-08-7]. More extensive data are available (27, 28).

Table 7. Formulation of Semipermanent Hair Dye Product

Substance	CAS RegistryNumber	Wt %
dyes		1.500
triethanolamine	[102-71-6]	1.200
oleic acid	[112-80-1]	0.600
propylene glycol	[57-55-6]	3.000
ethoxydiglycol	[111-90-0]	2.000
sodium lauryl sulfate	[151-21-3]	0.600
nonionic surfactant		2.500
hydroxyethylcellulose	[9004-62-0]	1.800
fragrance		0.300
water	[7732-18-5]	86.500

There is a wide variety of dyes unique to the field of hair coloring. Successive *N*-alkylation of the nitrophenylenediamines has an additive bathochromic effect on the visible absorption to the extent that violet-blue dyes can be formed. Since the simple *N*-alkyl derivatives do not have good dyeing properties, patent activity has concentrated on the superior *N*-hydroxyalkyl derivatives of nitrophenylenediamines (29, 30), some of which have commercial use (31). Other substituents have been used (32). A series of patents also have been issued on substituted water-soluble azo and anthraquinone dyes bearing quaternary ammonium groups (33).

Semipermanent hair color products are formulated at an alkaline pH, usually between 8.5 and 10. At this pH the cuticle of the hair lifts away from the hair a little, allowing for easier penetration of dye. An alkyl amine buffered with an organic acid normally is used to obtain the desired pH. The formulations contain a mixture of solvents and surfactants to solubilize the dyes and a thickening agent is added so that the product stays on the hair without running or dripping. A 20–30 min application time is normal for this type of product. A representative formula for a semipermanent dye product is given in Table 7.

Semipermanent hair color products have the advantage of being removable; if a consumer is not satisfied with the result, the color is gradually washed out of the hair. The products are perceived as very gentle. The ease of removal of these products is also a disadvantage because a consumer needs to reapply the color after every 6–8 shampoos to maintain the color.

The naturally derived dyes used by the Egyptians and other ancient civilizations are actually examples of semipermanent dyes. The best known dye of this kind comes from the Henna plant and is still in use after thousands of years. The extract of the Henna plant contains lawsone [83-72-7] (2-hydroxy-1,4-naphthoquinone). This dye produces a reddish color on hair, which is best used to produce a warming effect on brown hair. The dye is complicated to use in that it must be made into paste by mixing with hot water. The paste is then left on the hair for 30–45 minutes. Henna can enhance the color of brown hair by adding warm tones but the color on gray hair is an unattractive orange shade. Other dyes extracted from natural materials include chamomile, indigo, logwood, and walnut. Although all these materials can be used to dye hair, only henna is permitted in the United States as a hair colorant (ca 1993). Products using natural dyes other than henna are occasionally seen in the marketplace, but because of the lengthy application times and weak color results they are never very successful.

4.3. Permanent Hair Colorants

Permanent colorants produce hair coloration that lasts until the hair grows out. Color is formed inside the hair by hydrogen peroxide-induced coupling reactions of colorless dye precursors. A full range of shades can be obtained with this system and the permanent or oxidative hair colorants are considered to be the most important class of hair dyes.

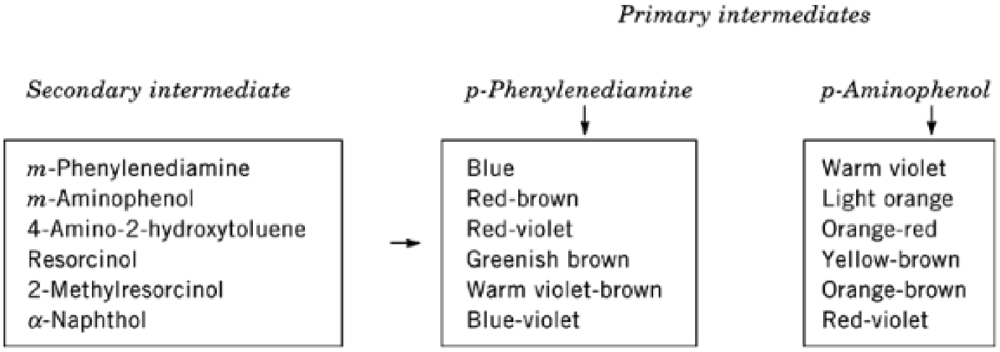

Fig. 1. Quinine imines from primary intermediates couple with secondary intermediates to form viscous colors.

4.3.1. Oxidation Hair Colorant

Color-forming reactions are accomplished by primary intermediates, secondary intermediates, and oxidants. Primary intermediates include the so-called para dyes, *p*-phenylenediamine, *p*-toluenediamine, *p*-aminodiphenylamine, and *p*-aminophenol, which form a quinone monoimine or diimine upon oxidation. The secondary intermediates, also known as couplers or modifiers, couple with the quinone imines to produce dyes. Secondary intermediates include *m*-diamines, *m*-aminophenols, polyhydroxyphenols, and naphthols. Some of the more important oxidation dye colors are given in Figure 1. An extensive listing is available (24, 28).

The mechanism of oxidative dyeing involves a complex system of consecutive, competing, and autocatalytic reactions in which the final color depends on the efficiency with which the various couplers compete with one another for the available diimine. In addition, hydrolysis, oxidation, or polymerization of diimine may take place. Therefore, the color of a mixture cannot readily be predicted and involves trial and error. Though oxidation dyes produce fast colors, some off-shade fading does occur, particularly the development of a red tinge by the slow transformation of the blue indamine dye to a red phenazine dye.

Also present but not essential in permanent hair colorants are nitro dyes which dye hair without oxidation. These dyes, nitro derivatives of aminophenols and benzenediamines, impart yellow, orange, or red tones. Although they have good tinctorial value, they are not as colorfast as the oxidative dyes. They also are used in semipermanent hair colorants.

Attempts to broaden the range of materials available as dye precursors have been made (34, 35). Oxidative dyes based on pyridine derivatives produce less sensitization than those based on benzene derivatives (36); however, they lack tinctorial power, lightfastness, and availability. Derivatives of tetraaminopyrimidine are claimed to act as primary intermediates to give intense shades with good fastness and excellent toxicological properties (37).

Oxidative hair dye products usually are formulated at a pH of 9.5–10.5. Ammonia, buffered with oleic acid, is the most commonly used alkalizing agent. Formulations contain a mixture of solvents and surfactants to solubilize the dyes and help in wetting the hair. A reducing agent is included in the formula to prevent premature oxidation of the dyes during storage. A typical formulation for a permanent hair color product is given in Table 8.

The colorant formulation is mixed just before application with an oxidizing agent, ie, developer. Hydrogen peroxide is the preferred developer usually at a concentration of 6%. An important function of hydrogen peroxide apart from inducing the color formation is the bleaching of the melanin pigment which constitutes the natural hair color. This process allows the development of light shades which are not available either with semipermanent or temporary dyes. Although the amount of lightening is limited, it is possible to dye hair one to two levels lighter. Thus dark brown hair can be lightened to light brown and light brown to medium blonde.

Table 8. Permanent Hair Colorant Formulation for a Medium Brown Shade

Ingredients	CAS RegistryNumber	Wt %	Function
oleic acid	[112-80-1]	15	surfactant
sodium lauryl sulfate	[151-21-3]	1	surfactant
oleyl alcohol	[143-28-2]	10	thickener
ammonia	[7664-41-7]	2	alkali
isopropyl alcohol	[67-63-0]	10	solvent
propylene glycol	[57-55-6]	5	solvent
sodium sulfite	[7757-83-7]	0.2	antioxidant
EDTA	[60-00-4]	0.05	sequesterant
p-phenylenediamine	[106-50-3]	0.7	reactant
resorcinol	[108-46-3]	0.4	reactant
1-naphthol	[90-15-3]	0.1	reactant
p-aminophenol	[123-30-8]	0.05	reactant
m-aminophenol	[591-27-5]	0.1	reactant
water	[7732-18-5]	55.4	

If lighter colors than these are desired it is necessary to decolorize all the melanin in the hair in a preliminary step, and then add color back to the desired depth in a second treatment. This is known as a double-process treatment. The decolorization step consists of treating the hair with an alkaline mixture of persulfate salts and peroxide. The persulfate is added to the peroxide as a dry powder immediately before applying to the hair. Although the persulfate salts alone do not have any bleaching effect, the persulfate–peroxide mixture can remove all the melanin in the hair. Dark brown or darker hair can be lightened to a light blonde shade in about an hour.

After the hair is bleached it has an unnatural straw-like color and is then dyed to the desired tone with either a semipermanent or a permanent hair color product. The dye products designed to color bleached hair to a natural looking blonde shade are called toners.

The presence of ammonia and hydrogen peroxide in permanent hair color products is a disadvantage. Both are considered by consumers to be harsh chemicals. The odor of ammonia is unpleasant for a personal care product. Monoethanolamine has been used as a substitute for ammonia in some commercial permanent hair color products. It is not as effective as ammonia in allowing the hair to be lightened but it does not have as strong an odor.

4.3.2. Longer Lasting Semipermanent Hair Dyes

Several products have appeared on the market that are positioned as being more gentle than the usual permanent hair color products. They use the same dyes as other permanent hair color and also are mixed with hydrogen peroxide immediately before use. They differ from other permanent hair dye products in that they employ an alkalizing agent other than ammonia to obtain a pH about one unit lower than conventional products. Sometimes they use lower concentrations of peroxide. Typically the color results obtained using these products are not as durable as the products formulated at a higher pH. These products are positioned as longer lasting semipermanent hair color products.

4.3.3. Melanin Drying

One development (ca 1993) in hair coloring involves the formation of pigments within the hair that are very similar to natural melanin. Thus either catalytic or air oxidation of 5,6-dihydroxyindole [3131-52-0] can be effectively used to permanently dye hair within a short time (38). The formed color can, if required, be further modulated with dilute H_2O_2 or can be even totally removed from hair by this oxidant.

4.3.4. Metallic Dyes

Metallic dyes are among the older hair color materials known. Commercial products are based on a 1% solution of lead acetate in an aqueous, slightly acidic, alcoholic medium. Precipitated sulfur appears to be essential. The convenience aspect is stressed by the leave-in application method. Actually, the color development is so slow, taking about a week to ten days, that there is no alternative to this technique. Daily application is needed at first.

It has been shown that keratin [9008-18-8], and not cellulose-type fibers, are dyed. It is speculated that a lead–sulfur–keratin complex is formed. The color penetrates the hair fiber to a limited extent, forming a ring around the outside edge and imparting a lifeless appearance. Once developed, the color cannot be removed. The shades are limited yellows or light browns. Appealing mainly to men, the products are often called color restorers because of the gradual build-up of color.

Although lead acetate [301-04-2] is the only metallic dye used in the early 1990s, salts or silver, copper, nickel, cobalt, bismuth, and iron have been utilized in the past. A patent (39) refers to the use of bismuth citrate in a solution made alkaline with triisopropanolamine.

4.3.5. Hair Bleaching

Hair owes its natural color to the internal deposits of melanin pigment, distributed in the form of granules (0.3 by 1 μm) within the hair cortex. The density of the pigment distribution together with the chemical nature of the pigment, ie, eumelanin, phaeomelanin, or both, determine the actual hair color. The purpose of bleaching is to lighten or altogether decolorize the natural pigment with minimal damage to the hair itself.

When hair is bleached, the physicochemical character of melanin undergoes profound alterations, resulting in a predictable change of hair color. Black or brown hair progressively changes to reddish brown, auburn, reddish blonde, and finally pale blonde. The process may be stopped at any point or continue to the lightest shade. The latter provides a good background for a variety of blonde shades that can be obtained in a subsequent coloring step. This bleaching and coloring combination is known as double-process blonding.

An ammoniacal solution is added just before use to activate the hydrogen peroxide. Ammonia is preferred over sodium carbonate (40) or ethanolamines for maximum bleaching. The alkaline solution can be formulated into a shampoo vehicle with oleate soaps or ethoxylated fatty alcohols. When the bleach is applied to areas such as new hair growth, a viscous cream or paste may be preferred, formulated with fatty alcohols, alkanolamides, or other thickeners.

Bleaches of the simple ammoniacal peroxide type give limited lightening, which can be increased with bleach accelerators or boosters, including one or more per salts such as ammonium, potassium, or sodium persulfate or their combinations. These salts, which are susceptible to decomposition in aqueous solution, are packaged as dry powders and added just before use. In the absence of hydrogen peroxide, however, persulfates do not have any bleaching effect (41).

The amount of oxygen evolved is not related to the degree of bleaching (40). Oxidative decoloring is caused by hydrogen peroxide or by the HO_2^- ions present in alkaline solution. Hydrogen peroxide is also an effective solvent for melanin (41).

In the reaction of alkaline hydrogen peroxide with keratin (41, 42), the disulfide cross-links of cystine are oxidized to sulfonic acid groups. This causes the hair to lose a portion of its tensile properties during bleaching. Despite these changes, the hair fibers retain their integrity and the results are usually pleasing to the user. However, care must be taken during repetitive applications to limit the bleach mixture to the regrowth, especially when persulfates are used. To this end it is important to employ high viscosity mixtures with minimum tendency to spread onto previously bleached hair.

4.4. Hair Coloring Regulation Issues

In the United States the classification of color additives is complex. Under the Federal Food, Drug and Cosmetic Act, all cosmetic colors must be the subject of an approved color additive petition to the Food and Drug Administration; there is an exception for coal-tar colorants used to color hair. Based on the composition of these colorants, FDA can require a certification on each manufactured batch of colorant to assure conformance with the approved specifications. In the early 1990s FDA has required certification only for synthetically derived coal-tar type colors. Many of the approved color additives, both certified and noncertified, are restricted in their potential use. These restrictions can be found in the color additive regulations in the Code of Federal Regulations at 21 CFR 73 and 74.

Any of these approved color additives may also be used to color the hair as long as they are not specifically restricted from this use. However, as noted before, there is an exception to the use of coal-tar colorants to color hair. This exception, which further complicates the regulation of colorants, is due to the presence of the so-called hair dye exemption in the Federal Food, Drug and Cosmetics Act. When this Act was passed in 1938 and again when the Color Additive Amendments of 1960 were enacted, U.S. Congress recognized the sensitizing potential of some hair colors and specifically separated the use of coal-tar colors for coloring hair from the adulteration and color additive provisions of the law. However, in order to use these coal-tar colors, Congress did provide for specific warnings and conditions for their use. Nowhere in the Act, however, did Congress define coal-tar colors. FDA has interpreted this term to mean colors synthetically derived from aromatic chemical sources. They have recognized that the term coal-tar in the Federal Food, Drug and Cosmetics Act is a generic term that describes the original synthetic sources of these dyestuffs and is not meant to be restrictive as to the specific organic feedstock. Most coal-tar colors used in 1993 are derived from petrochemicals.

Based on the lack of a definition for coal-tar colors in the Act, and on a liberal interpretation of Section 601(e) (43), many materials have been used to color hair under this exemption. The use of coal-tar color for coloring hair was clarified by a ruling of the United States Court of Appeals for the second circuit in Toilet Goods Association v. Finch in 1969 and by a subsequent notice in the *Federal Register* (44). Under this ruling the Court stated that Congress did not intend to exempt noncoal-tar colors from Section 601(e). The notice further states that metallic salts and vegetable substances are not coal-tar derivatives and their use for coloring hair, without an approved color additive petition, would be considered adulteration. Following this Notice, petitions for henna, bismuth citrate, and lead acetate were approved by FDA for use in coloring hair. These materials are the only vegetable materials and metallic salts that can be used (ca 1993) to color the hair and are restricted for use.

Lead acetate can be used only for coloring scalp hair at a level not to exceed 0.6%, as lead, weight/volume of the product. The regulations provide specific restrictions (including label specifications) that lead acetate must not be used to color mustaches, eyelashes, eyebrows, or hair on parts of the body other than the scalp.

Bismuth citrate can be used only for coloring scalp hair such that the amount of bismuth citrate does not exceed 0.5% weight/volume of the product. Specific restrictions prohibit the use of bismuth citrate for coloring eyelashes, eyebrows, or hair on parts of the body other than the scalp; they also indicate label specifications.

Henna can be used only to color hair with the exception of eyelashes, eyebrows, or generally in the area of the eye. The label for products containing henna must caution the consumer not to use in the area of the eye or on cut or abraded scalp.

The use of nonapproved coal-tar colors for coloring hair does require special warnings and precautions; a cosmetic is deemed adulterated if it bears or contains any poisonous or deleterious substance which may render it injurious to users under the conditions of use (43). Coal-tar hair dye is exempt if the label conspicuously contains a warning that the product contains ingredients which may cause skin irritation on certain individuals, that a preliminary test according to accompanying directions should first be made, and that the product must not be used for dyeing the eyelashes or eyebrows; to do so may cause blindness. In addition, the labeling must include directions for doing the preliminary patch test. It should be noted, however, that the hair dye exemption for coal-tar dyes relates only to coal-tar dyes not listed as approved color additives. The certified colors approved by FDA for use in cosmetics are also coal-tar colors. The use of those specific coal-tar dyes for coloring hair does not require the warnings and patch test instructions (43).

5. Permanent Waving Preparations

The interest in and appreciation of the beauty of waved hair were shared already by ancient Assyrians who, as depicted on numerous base reliefs, wore cascades of curls falling over their shoulders. Little is known of the technology used at that time to produce their curls but it may not have been different from the waving techniques employed by Egyptians who curled their hair with mud and then dried it in the hot sun. Since then, improvements in waving techniques have been associated with the progress of technology; these historical developments are well documented (45, 46). Basic precepts of modern permanent waving are due to pioneering work in the 1930s on the chemical and physical properties of wool (47, 48). Over the years, these principles have been creatively utilized and adapted by cosmetic chemists to yield safe and efficacious products enjoyed by millions of consumers every year.

5.1. Chemistry of Hair Waving

A particular geometry innate to each individual hair is the result of processes of keratinization and follicular extrusion that transform viscous mixtures of polypeptide chains into strong, resilient, and rigid keratin fiber. Waving entails softening keratin, molding it to a desired shape, and finally annealing the newly imparted configuration. The underlying mechanism of waving is thus essentially molecular and involves a manipulation of physico-chemical interactions that stabilize the keratin structure.

In native keratin the conformation stability is derived primarily from covalent cross-linking by cystine and from an extensive network of hydrogen bonds. Some contribution also comes from the electrostatic interaction of basic and acidic side chains, ie, salt linkages, as well as from the hydrophobic bonding on nonpolar residues present in keratin; however, the contribution of the latter is small, and in the intact fiber the covalent and polar interactions greatly overshadow the nonpolar ones. The hydrogen bonds, although weaker than either the disulfide cross-links or salt bridges, are much more numerous, ie, an average of 10 hydrogen bonds per each disulfide or salt link, and are largely responsible for the dry strength and rigidity of hair. Water readily breaks hydrogen bonds and this plasticizing action is utilized in imparting a temporary wave (set) to hair. The process is simple, being accomplished by wrapping wet hair around a roller or rod and drying it in the curled state. On drying, hydrogen bonds are reformed in a new configuration which is additionally stabilized by the recovery of fiber stiffness. Exposure to moisture quickly reverses the setting process and the hair returns to its natural shape.

Attempts to obtain permanent waving effects by manipulation of secondary bonds alone, ie, hydrogen bonds, salt-linkages, or nonpolar interactions, have proved unsuccessful. The cleavage of covalent disulfides in addition to secondary bond rupture is essential for imparting a durable wave stable to repeated shampooing (48). The cystine cross-links play the dominant role in controlling the recovery process in fiber. Severance of at least some of these cross-links is necessary to allow for molecular rearrangement, and some degree of molecular flow, that must take place during the molding step to attain relaxation of imposed stress and effective rebuilding of stabilizing bonds. Reductive fission of hair disulfides by mercaptans has become the preferred technique.

$$\text{keratin—S—S—keratin} \rightleftarrows 2\text{keratin—SH}$$

Under relatively mild conditions, adequate cleavage can be achieved and the ensuing formation of cystine residues provides a welcome opportunity to reform the severed linkages by simple oxidative treatment to complete the process cycle. The reduction usually is carried out under alkaline conditions which favor the generation of the attacking nucleophile or mercaptide ion; potentiate the swelling of keratin; and promote the molecular rearrangement via sulfhydryl–disulfide interchange.

A viable alternative to reduction fission is the sulfitolysis of hair. The action of sulfite on the combined cystine in keratin yields one cystine residue and a Bunte salt. The reaction is highly reversible, particularly at pH 8. This feature of reversibility associated with limited fission of disulfide cross-links renders the waving with alkali sulfite simple and less aggressive than that with thioglycolic acid [68-11-1]. The attained curl is more of a body wave type. Higher cleavage levels, similar to those obtained with mercaptans, can be generated at neutrality but this downward shift in pH impairs the molecular rearrangement process and manifests itself in a softer and less durable wave.

The final step of the permanent waving reforms the disulfide bonds; it is usually called neutralization. To rebuild a disulfide cross-link in hair from two residues of combined cysteine [52-90-4] requires a close proximity of the reacting side chains. Interfering factors are numerous, yet the rebuilding reaction is very effective. Attesting to this is evidence of the recovery of the mechanical strength of the fiber and direct analysis of combined cystine [56-89-3] prior to and after neutralization. Data suggest that between 80–90% of the cysteine residues formed during the reduction step are converted back into cystine upon neutralization (49, 50). It is not known what happens with the remaining 10–20% of the residues. Excluding dithiodiglycolic acid, cysteic acid residues seem to be the only identified by-products of the neutralization reaction. The latter are formed, however, in quantities too small to account for the balance of lost cysteine.

5.1.1. Hair Waving Process

In the typical waving procedure, freshly shampooed and still damp hair is divided into 40–60 tresses. Each tress is wetted with waving lotion and wound onto plastic curlers with the help of porous end papers or sponges. The size of the curler decides the nature of the resultant wave. The smaller the curler, the tighter the wave. Hair is then left to process, rinsed thoroughly after 10–20 min, and neutralized while still on rods. After neutralization, hair is unwound, rinsed again, and either freely dried or set in the desired style.

Depending on the type of waving product used, there may be several variations to the procedure outlined above. Thus, instead of wrapping with lotion, the hair is wound wet and the lotion applied to curled hair. Some instructions also suggest a creep stage for better tightness and durability. This is simply a 30 min wait between rinsing off the lotion and application of the neutralizer.

5.2. Waving Lotions

The reagent most frequently used for the reduction of hair is thioglycolic acid [68-11-1]. Although a variety of other mercaptans have been screened (51), none has been able to match the unique combination of efficacy, safety, and low cost that is a hallmark of thioglycolic acid.

Conventional waving lotions contain 0.5–0.8 M thioglycolic acid adjusted to and maintained at pH 9.1–9.5. The neutralizing base is ammonia [7664-41-7], alkanolamines, or both. Ammonia appears more effective than sodium hydroxide [1310-73-2] in facilitating diffusion of the thioglycolate through the hair. It is also preferred over nonvolatile amines because it escapes during processing. The resultant drop in pH reduces the activity of the lotion with time and thus minimizes the danger of over processing. Under practical waving conditions, ammonium thioglycolate [5421-46-5] fully penetrates the hair in 15–20 min (49, 50, 52), although longer time may be required for very coarse hair (1). The extent of disulfide bond cleavage that typically occurs during waving varies between 20–40% (53), the lower figure being a representative value for previously untreated hair.

Alkali sulfites have gained a stronghold in the hair waving market, focusing on the soft wave and casual styles for which the expectations of the waving performance are less rigorous. Reduced danger of over processing and lack of odor are clear benefits. Both ammonium sulfite [10196-04-06] and sodium sulfite [7757-83-7] are used in concentrations ranging from 0.5–1.0 M at pH 6.5–10.2 (54, 55).

Waving products have appeared on the market formulated in the neutral pH range, ie, so-called acid waves. They are based either on the thioglycolic acid or its glyceryl esters. The waving performance of these products is mediocre. The resulting wave lacks the crispness and durability of the conventional alkaline wave although this is somewhat compensated by lower hair damage. Often heat is used to improve the result.

In the Orient, particularly Japan, the use of cysteine as a waving agent is widespread. This amino acid is claimed to provide a natural and nonodorous alternative to thioglycollic acid and to wave the hair without the damage. As a waving agent cysteine is a poor performer and, in most formulations, thioglycolic acid is added to improve waving efficacy.

Waving lotions frequently are formulated with a number of additives with the intention of enhancing the efficacy and the aesthetics of the process. Thus surfactants of the nonionic type are used to improve the wetting of hair and penetration, a hydrogen bond breaking agent such as urea [57-13-6] is added to intensify the swelling of hair, ammonium sulfate [7783-20-2] is used to decrease swelling, and latex emulsions and polyacrylates are employed as opacifiers. Conditioning materials used include mineral oil [8012-95-1], lanolin [8020-84-6], and hydrolyzed protein; the addition of cationic polymers has been patented (56, 57). Perfuming of the thioglycolate lotions, although essential and desirable, is very difficult as the odor of the mercaptan is augmented by the unpleasant smell of the reduced hair. The latter is particularly evident in the case of sulfite lotions which are usually odorless.

5.3. Neutralizing Lotion

The principal active ingredient of cold wave neutralizers is usually an oxidizing agent. The most popular is hydrogen peroxide [7722-84-1], employed at a concentration of 1–2%; it continues to find widespread use. Aqueous solutions of sodium bromate [7789-38-0] at a concentration of 10–20% occasionally are used and are technically preferred over the peroxide formulations because of excellent stability and absence of hair bleaching. Neutralizing powders appear to be on the decline but formulations still in use consist of sodium perborate [7632-04-4] combined with hexametaphosphates to improve solubility in hard water.

Wetting and foaming additive agents occasionally are used to improve spreading and retention of the neutralizer in the hair. Acids such as citric acid [77-92-9] and tartaric acid [526-83-0] are suggested for the deswelling of hair and thus improvement in its overall condition. Conditioning agents such as stearalkonium chloride [122-19-0] are frequently employed to assure smooth texture, easy combing, and control of flyaway. Conditioning additives based on polymeric silicones have been patented (58).

5.4. Evaluation

Two parallel approaches are used in the industry to assess the efficacy of waving formulations. These are full- and half-head tests against established products, and laboratory evaluation of hair tresses processed according to waving instructions. The latter consists of a battery of tests related to the waving performance of the product, eg, degree of curl, durability of curl to repeated shampooing, etc; incidental hair damage, ie, measurements of swelling and tensile strength; and the final hair condition, ie, assessment of luster, dry and wet combability, and flyaway. Descriptions of laboratory techniques used in context of these tests have been published (59–62).

5.5. Health and Safety

The dermal toxicology of alkaline solutions of thioglycolic acid has been reviewed extensively (63–65). The reagent has been found harmless to normal skin when used under conditions adopted for cold waving. Some irritation is observed on abraded skin but this appears to be associated with the alkaline component of the waving solution (65). Hand protection is recommended for the professional hairdressers who routinely handle these products.

5.6. Manufacturing

The highly reactive nature of the active components of the permanent waving products requires rigorous control at every production stage. Cleanliness must be exemplary. Metal contaminants must be avoided and all tanks, valves, hoses, and bottling-machine parts in contact with the chemicals must be inert or lined with glass or nonreactive plastic (Teflon, polyethylene). Only high purity materials should be used and must be adequately checked prior to manufacture.

6. Hair Straightening Preparations

There are functionally different types of hair straightening preparations, ie, those which produce temporary straightening and those which are designed to accomplish permanent effects.

6.1. Temporary Hair Straightening

The most frequently used technique in this category is hot combing. An oily substance, ie, pressing oil, is applied to hair which is then combed under tension with a heated comb. The function of the pressing oil is to act simultaneously as a protective heat-transfer agent between the comb and the hair and as a lubricant to reduce the drag of the comb. The straightening effect is immediate but is lost quickly on exposure of hair to moisture. Pressing oils are usually based on petrolatum [8027-32-5] and mineral oil mixed with some wax and a perfume. Frequent hot combing dulls and damages the hair and leads ultimately to hair breakage.

6.2. Permanent Hair Straightening

The basic technical premise underlying permanent hair straightening is similar to that adhered to in waving. Hair is softened; maintained straight under tension for a period of time, usually accomplished by means of the high viscosity of the product and repeated combing; rinsed; and rehardened by application of the neutralizer. It thus is not surprising that many hair straightening compositions are just thickened versions of permanent waving products. Alkaline thioglycolate (6–8%) is formulated into a thick oil-in-water (o/w) emulsion or cream using generous concentrations of cetyl alcohol [124-29-8] and stearyl alcohol [112-92-5] and high molecular weight polyethylene glycol, together with a fatty alcohol sulfate as emulsifier. The emulsifier provides an added advantage of ready rinsability. Processing time may be anywhere from 30 min to 2 h, depending on the initial curliness of the hair. Conventional oxidizing neutralizers, eg, H_2O_2, bromates, and perborates, are used in the final step of the process.

Hair straightening compositions based on mixtures of ammonium bisulfite [10192-30-0] and urea [57-13-6] have been introduced and have found some application in the Caucasian hair market. The reformulation of the cystine cross-links in bisulfite-reduced hair is best accomplished by a rinse, pH 8–10, rather than by the use of oxidizing agents (66).

An important class of permanent straighteners in use is that based on alkali as an active ingredient. Sodium hydroxide [1310-73-2], potassium hydroxide [1310-58-3], or a sodium carbonate [496-19-8] combination with guanidine [593-85-1] are used at concentrations of 1.5–3% in a heavy cream base. Even though the recommended treatment time is only between 5 and 20 min, the straightening effects, in general, surpass those obtained with either thioglycolates or bisulfites. This is due to the very different chemistry of the process as well as greater aggressiveness of the alkaline relaxers. A 15 min treatment irreversibly decreases the cystine content of hair to two-thirds of its initial value (2). The damaging action of strong alkali on hair is not restricted to the disulfide bonds alone. Apart from the potential of the main chain scission, ie, peptide bond hydrolysis, the very nature of the high pH base leads to a build-up of negative charges in hair which results in increased swelling, the latter being intensified by concurrent breakdown of the disulfide bonds. Great care must be exercised in the use of the alkaline relaxers as even a short contact with skin can cause blistering.

7. Professional Use Products

Many products in the hair care and hair color categories are distributed solely for professional use by cosmetologists, beauticians, and hairdressers in their places of business.

The Fair Packaging and Labeling Act does not apply to products used in professional establishments. Specifically, this means that these products are not required to have an identity statement or a list of ingredients. This exception, however, is limited only to those products actually intended for professional use. Products sold by the professional establishments to their customers for personal use are considered retail products and must be fully labeled as such.

Although these professional-use-only products do not require ingredient labeling, the cosmetics industry has developed a program to voluntarily list the components of professional products. However, under this voluntary program, the ingredients are listed in alphabetical order rather than descending order. This has been done to make it easier for the professional hairdresser to locate a specific compound that may be of interest.

8. Economic Aspects

Retail sales of hair preparations have more than doubled from $\$2 \times 10^9$ in 1978 to ca $\$4.2 \times 10^9$ in 1991 (67). While price increases over this 13-year period were clearly a factor, a variety of novel and functional products have been introduced into this market. A large rise in the shampoo sales, from $\$777 \times 10^6$ in 1978 to $\$1510 \times 10^6$ in 1991, was helped by the new and highly effective category of conditioning shampoos. However, conditioning shampoos had little adverse effect on the conditioner market which exploded from sales of $\$121 \times 10^6$ in 1978 to well over $\$800 \times 10^6$ in 1992. Diversification and new product lines in the hair styling category, particularly styling mousses, have pushed sales from $\$327 \times 10^6$ in 1978 to $\$870 \times 10^6$ in 1991. Permanent waves generated renewed appeal to consumers by growing from $\$39 \times 10^6$ in 1978 to well over $\$120 \times 10^6$ in 1992. There has been some growth in hair coloring, helped primarily by introduction of products for men, with total sales in 1992 of $\$571 \times 10^6$ as compared to $\$300 \times 10^6$ in 1978.

9. Regulations

9.1. Definitions

Cosmetic products in the United States are regulated by FDA under the authority of two different laws, ie, the Federal Food, Drug and Cosmetics Act and the Fair Packaging and Labeling Act. Each of these Acts imposes slightly different conditions and labeling requirements for the products under their jurisdiction.

The Food, Drug and Cosmetics Act defines a cosmetic as a substance intended to be rubbed, poured, sprinkled, or sprayed on, introduced into, or otherwise applied to the human body or any part thereof for cleansing, beautifying, promoting attractiveness, or altering the appearance. A drug is defined as an article intended for use in the diagnosis, cure, mitigation, treatment, or prevention of disease in humans or other animals, and articles intended to affect the structure or any function of the body of humans or other animals.

The Fair Packaging and Labeling Act, which uses the same definitions for drugs and cosmetics as the Food, Drug and Cosmetic Act, only has jurisdiction over retail products sold to the consumer for use at home. This condition exempts free samples and professional use products not sold to a consumer for personal use.

9.2. Labeling Regulations

The Food, Drug and Cosmetics Act requires that the cosmetic product be safe under conditions of use and that labeling is not false or misleading. Under this Act, the labeling of a cosmetic product must contain the name and address of the manufacturer, packer, or distributor; the net contents; and any appropriate warnings. This information must appear on the label of the product, both inner and outer containers.

The Fair Packaging and Labeling Act is designed to provide the consumer with information to help them make value comparisons in the marketplace. It requires the name and address of the manufacturer, packer, or distributor; the net contents; an identity statement of the function of the product; and for cosmetics, a listing of the ingredients in descending order of concentration. The above information must appear only on the outer label; the identity statement and the ingredient labeling need not appear on inside packaging, if there is any. These items are only mandatory on the outside package where the consumer can see them at point of purchase. Since both acts require the name and address of the manufacturer, packer, or distributor, and the net contents, these items must appear on all labeling copy.

Labeling compliance with these regulations is complex, and further labeling information is available (67, 68).

9.3. Drug Products

Although most hair care products are cosmetics and are regulated as such, some products also can be drugs. The regulatory status of these products is determined by the intention or claims made for the product. If the product is intended simply to beautify, cleanse, or alter the appearance, the product is a cosmetic. If, however, the product is intended to treat or prevent a disease condition or to affect the structure or function of the body, the product is a drug. Therefore, any product that makes a representation that it can control dandruff, treat psoriasis or seborrheic dermatitis, grow hair, prevent baldness, or other similar claims, is considered a drug product. Products that make both drug and cosmetic claims are considered drugs and must be in compliance with both the drug and cosmetic regulations.

Drug products must meet the requirements established by the Center for Drug Evaluation and Research at FDA. They must comply with the appropriate OTC Drug Review Final Rule published in the *Federal Register* or must be the subject of an approved New Drug Application (NDA) filed with FDA. Products not meeting these requirements are considered by FDA to be New Drugs without an NDA and subject to regulatory action.

FDA has published two final rules for hair products as of this writing (69). Any over-the-counter (OTC) drug product labeled or promoted for external use as a hair grower or for hair loss prevention is regarded as a new drug and must be the subject of an approved new drug application (NDA). Products making these claims without an NDA are considered to be in violation of the Federal Food, Drug and Cosmetic Act and are also mislabeled.

The conditions whereby dandruff, seborrheic dermatitis, and psoriasis drug products are generally recognized as safe and effective and are not misbranded is available (70). Specific active ingredients that can be used as well as the statement of identity, indications for use, and required warnings, are identified. Products that do not meet all of these requirements are considered new drugs and must have an approved NDA for the nonmonograph conditions.

There are a variety of other regulations and restrictions that affect all cosmetics including hair products. At the federal level, there are required warnings and restrictions for aerosol products and for products where safety has not been adequately substantiated (71). Other issues have been generally initiated by various state governments. California Proposition 65 contains warnings for products that expose consumers to specified levels of chemicals that cause cancer or reproductive toxicity. Many states, including California, New York, Rhode Island, and Vermont, have enacted legislation that restricts product environmental claims including degradability, recycling issues, and environmental safety. The Federal Trade Commission has issued guidelines for environmental claims but these may not be sufficient to meet the requirements of all the states. Several states, notably California and New York, have enacted legislation limiting the amount of volatile organic compounds (VOCs) in various product types, including hair sprays and other hair care products. For hair mousses the level of VOCs must not exceed 16% by January 1, 1994, and for hair styling gels that level must not exceed 6% by January 1, 1997.

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STANLEY POHL
JOSEPH VARCO
PAUL WALLACE
LESZEK J. WOLFRAM
Clairol, Inc.

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