COSMETICS

1. Introduction

Cosmetics are products created by the cosmetic industry and marketed directly to consumers. The cosmetic industry is dominated by manufacturers of finished products but also includes manufacturers who sell products to distributors as well as suppliers of raw and packaging materials. Cosmetics represent a large group of consumer products designed to improve the health, cleanliness, and physical appearance of the human exterior and to protect a body part against damage from the environment. Cosmetics are promoted to the public and are available without prescription.

The difference between a cosmetic and a drug is often confusing. In the United States the inclusion of a drug constituent, as defined by the Food and Drug Administration (FDA), in a cosmetic product may make the product a drug; whenever there is a claim for pharmacological activity of one of a product's constituents, the product is a drug. Some products are identified as quasi or over-the-counter (OTC) drugs according to each country's regulations. The composition, claim structure, and distribution of OTC products may be more tightly regulated than those of pharmacologically inactive cosmetics. The difference between an ordinary cosmetic and a quasi or OTC drug may not be readily apparent; it is based on statutory regulations. Certain types of products, such as hair-growth products and skin rejuvenators, are not cosmetics, and OTC claims for hair growth or skin rejuvenation are not allowed in the United States.

Cosmetics, regardless of form, can be grouped by product use into the following seven categories: (*1*) skin care and maintenance, including products that soften (emollients and lubricants), hydrate (moisturizers), tone (astringents), protect (sunscreens), etc, and repair (antichapping, antiwrinkling, antiacne agents); (*2*) cleansing, including soap, bath preparations, shampoos, and dentifrices (qv); (*3*) odor improvement by use of fragrance, deodorants, and antiperspirants; (*4*) hair removal, aided by shaving preparations, and depilatories; (*5*) hair care and maintenance, including waving, straightening, antidandruff, styling and setting, conditioning, and coloring products (see HAIR PREPARATIONS); (*6*) care and maintenance of mucous membranes by use of mouthwashes, intimate care products, and lip antichapping products; and (*7*) decorative cosmetics, used to beautify eyes, lips, skin, and nails.

2. History

Cosmetic preparations and usage are rooted in antiquity, when suspensions of natural pigments in lipids were evidently used to enhance appearance, and fragrant plant concoctions were widely traded. The use of cosmetics for adornment is recorded in biblical writings, and the use of soap (qv), probably a hydrolysate of animal lipids by wood ashes, was encouraged for cleanliness. The benefits of bathing were fully known to the ancients, who built elaborate bathhouses. Bathing became less popular in Western cultures during the Middle Ages but again became accepted during the eighteenth and nineteenth centuries.

Kirk-Othmer Encyclopedia of Chemical Technology.

The use of fragrant substances has been continuous, and the use of lipids or emollients for anointing is fully documented in historical writings. However, it is probably not justifiable to identify the recipes passed on from antiquity as cosmetics. The compositions based on folklore and mysticism were replaced by more scientifically acceptable products beginning about 1875. The first edition of a handbook of cosmetic chemistry published in 1920 included a foreword noting that scientific cosmetic chemistry did not exist prior to that publication (1). A few years later, texts on cosmetic chemistry and other formularies became available (2).

The Society of Cosmetic Chemists, with individual memberships, was founded in the United States after World War II, based on the belief that scientific expertise and exchange were the foundations for future expansion of the cosmetic industry. Prior to that time, knowledge of cosmetic formulation was jealously guarded. Related scientific societies emerged in other countries and have since joined to form the International Federation of Societies of Cosmetic Chemists.

3. Economic Aspects

Economic summaries of the cosmetic industry, commonly documented by sales volume, are sometimes based on unit sales, sometimes on manufacturers' sales in monetary units, and sometimes on consumer spending. Figures normally include contributions by private labeling operations but do not necessarily reflect the value of the industry service sector, which includes suppliers of raw materials, beauticians, testing laboratories, and other specialists. Moreover, product categories cannot be rigidly defined. For example, the differentiation between a deodorant (a cosmetic) and an antiperspirant (an OTC drug) is often obscured by its trade name.

A summary by broad categories is given in Table 1. A more detailed breakdown of U.S. cosmetic sales is provided in Table 2. The U.S. Commerce Department reports a modest (8%) increase in the value of cosmetic industry shipments between 1989 and 1991, despite a 13% decrease in total industry employment.

Numerous cosmetic trade organizations exist. Foremost among them are the Cosmetic, Toiletry, and Fragrance Association (CTFA), formerly the Toilet Goods Association; the European Cosmetics Industries Federation (COLIPA);

Table 1. **U.S. Manufacturers' Sales of Cosmetics and Toiletries**[a]

	Annual sales, $\$ \times 10^6$		
Product line	1985	1990	Average annual growth, %
hair care	3,630	4,760	5.5
skin care	2,500	3,510	7.0
color cosmetics	2,540	3,380	5.9
fragrances	2,370	2,840	3.7
other toiletries	4,160	5,270	4.8
Total	15,200	19,760	5.4

[a] Courtesy of Kline & Company, Fairfield, N.J.

Table 2. **1991 U.S. Cosmetic Sales**[a]

Product line	Sales, $\$ \times 10^9$
hair care	5.10
fragrances	3.90
makeup (color)	3.00
skin care	1.80
antiperspirant and deodorants	1.60
dentifrices	1.20
mouthwashes	0.58
shaving	0.58
hair coloring	0.57
sun care	0.40
nail care	0.37
Total	20.00

[a] Based on U.S. Department of Commerce *Economic Industry Reports* and estimates by the staff of *Drug and Cosmetic Industry*.

and the Japanese Cosmetic Industry Association (JCIA). These organizations provide member companies with regulatory and technical information and supply documentation on the industry's practices to governments and consumers. The cosmetic industry supports a number of trade journals. Comprehensive annual listings of companies, individuals, and products are available (3–5).

4. Regulation of the Cosmetic Industry

In the United States, the 1938 revision of the Federal Food and Drug Act regulates cosmetic products and identifies these materials as:

(*1*) articles 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, and (*2*) articles intended for use as a component of any such articles, except that such term shall not include soap.

This definition establishes the legal difference between a drug and a cosmetic. It is clearly the purpose of, or the claims for, the product, not necessarily its performance, that legally classifies it as a drug or a cosmetic in the United States. For example, a skin-care product intended to beautify by removing wrinkles may be viewed as a cosmetic because it alters the appearance and a drug because it affects a body structure.

The FDA is responsible for enforcing the 1939 act as well as the Fair Packaging and Labeling Act. In light of the difficulty of differentiating between cosmetics and drugs, the FDA has in recent years implemented its regulatory power by concluding that certain topically applied products should be identified as OTC drugs. As a group, these OTC drugs were originally considered cosmetics and remain among the products distributed by cosmetic companies. They include acne, antidandruff, antiperspirant, astringent, oral-care, skin-protectant, and sunscreen products.

The use or presence of poisonous or deleterious substances in cosmetics and drugs is prohibited. The presence of such materials makes the product "adulterated" or "misbranded" and in violation of good manufacturing practices (GMP), which are applicable to drugs and, with minor changes, to cosmetics (6).

In contrast to prescription drugs, OTC drugs and cosmetics are not subject to preclearance in the United States. However, the rules covering OTC drugs preclude introduction of untested drugs or new combinations. A "new chemical entity" that appears suitable for OTC drug use requires work-up via the new drug application (NDA) process. In contrast, the use of ingredients in cosmetics is essentially unrestricted and may include less well known substances.

4.1. Color Additives. The FDA has created a unique classification and strict limitations on color additives (see also COLORANTS FOR FOOD, DRUGS, COSMETICS, AND MEDICAL DEVICES). Certified color additives are synthetic organic dyes that are described in an approved color additive petition. Each manufactured lot of a certified dye must be analyzed and certified by the FDA prior to usage. Color lakes are pigments (qv) that consist of an insoluble metallic salt of a certified color additive deposited on an inert substrate. Lakes are subject to the color additive regulations of the FDA and must be certified by FDA prior to use. Noncertified color additives require an approved color additive petition, but individual batches need not be FDA certified prior to use.

Hair colorants, the fourth class of color additives, may be used only to color scalp hair and may not be used in the area of the eye. Use of these colorants is exempt, that is, coal-tar hair dyes may be sold with cautionary labeling, directions for preliminary (patch) testing, and restrictions against use in or near the eye. The FDA diligently enforces the rules governing color additives and limits the use of, or even delists colorants deemed unsafe. The list of substances specifically prohibited for use in cosmetics is short.

Under the Fair Packaging and Labeling Act, the FDA has instituted regulations for identifying components of cosmetics on product labels. To avoid confusion, the CTFA has established standardized names for about 6000 cosmetic ingredients (7). Rigid U.S. labeling requirements mandate that ingredients be listed in order of descending concentration. Similar regulations are expected for European cosmetics within the next few years (8).

4.2. European Regulations. Regulations for cosmetics differ from country to country but, in general, are similar to or patterned after U.S. regulation. Thus, the identification of a cosmetic in the European Community differs only marginally from that in the United States. A 1991 European Economic Community (EEC) directive defines a cosmetic as:

> any substance or preparation intended for placing in contact with the various external parts of the human body (epidermis, hair system, nails, lips and external genital organs) or with the teeth and the mucous membranes of the oral cavity with a view to cleaning them, perfuming them, protecting them, keeping them in good condition, changing their appearance and/or correcting body odours.

EEC proposals also assert that cosmetic products must not damage human health when applied under normal or reasonably foreseeable conditions of use.

Finally, the EEC directive states that the label of a cosmetic should include a list of ingredients in descending order of weight at the time of manufacture.

Although the EEC is still in the process of completing cosmetic regulation, the final directive is expected to require member states to ban marketing of cosmetics that contain prohibited ingredients, an amount of a substance in excess of that proscribed, coloring agents, preservatives, or uv filters not specifically allowed.

4.3. Japanese Regulation. Japanese regulations of cosmetics are similar to those already discussed. The safety and quality of cosmetic products are regulated under the Pharmaceutical Affairs Law with detailed requirements for approval and licensing of manufacturing and import, for labeling and advertising standards, and for reporting safety data to the Ministry of Health and Welfare.

Cosmetics in Japan are defined as externally used articles for cleaning, beautifying, promoting attractiveness, and altering the appearance of the human body and for keeping the skin and hair healthy, provided that the action of the article on the human body is mild. Articles intended for use in diagnosis, treatment, or prevention of disease and those intended to affect the structure or any function of the body are identified as quasi drugs and are excluded. Japanese law identifies the following as quasi drugs: products for the prevention of foul breath or body odor; products for the prevention of prickly heat; products for the prevention of hair loss, promotion of hair growth, or removal of hair; hair dyes; agents for permanent waving of hair; and agents combining cosmetic effects with the purpose of preventing acne, chapping, itchy skin rashes, chilblains, or disinfection of the skin or mouth.

The Japanese regulations include both a list of substances that may not be used in cosmetics and a list of ingredients that may be used but which must conform to the specifications of the Japanese Standards of Cosmetic Ingredients. Some ingredients are allowed only in some types of cosmetic preparations. The use of certain hormones is controlled, and concentration limits exist for another group of ingredients. Japanese regulations differ significantly from U.S. regulations with regard to the formal recognition of an allowed, or positive, list.

Regulatory changes and discussions of the impact of regulations on the manufacture and import of cosmetic products are available in manuals published by the CTFA (9).

5. Product Requirements

5.1. Safety. Cosmetic products must meet acceptable standards of safety during use, must be produced under sanitary conditions, and must exhibit stability during storage, shipment, and use. Cosmetics are not lifesaving or life-prolonging drugs, and the requirements for innocuousness are absolute. In the United States the manufacturer bears the responsibility for not using injurious or questionable ingredients. The safety of each ingredient used in each finished cosmetic product must be adequately substantiated prior to marketing. In countries that have positive lists of ingredients that may be used in cosmetics, the burden for testing each finished cosmetic products is reduced. Positive listing assumes, without requiring evidence, that no adverse effects result from the use of a mixture of safe ingredients.

For many years the safety of cosmetic ingredients has been established using a variety of animal safety tests. More recently animal welfare organizations have urged that this type of safety testing be abandoned. Despite widespread use of cosmetics without professional supervision, the incidence of injury from cosmetic products is rare. In part, this is the result of extensive animal safety testing of components as well as of finished products. Such animal testing was considered mandatory from about 1945 to about 1985. Since the mid-1980s animal testing has been significantly reduced.

In vitro safety testing technology is becoming more common. Validation of these methods is based on comparisons with early animal safety data. Whether these *in vitro* tests can ensure the safety of all products that reach the consumer cannot be predicted (10). As of this writing, the principle that *in vitro* testing may be substituted for *in vivo* testing for complete safety substantiation has not been accepted by regulatory agencies. In the United States, the CTFA created the Cosmetic Ingredient Review (CIR) for the purpose of evaluating existing *in vitro* and *in vivo* data and reviewing the safety of the ingredients used in cosmetics. The review of ingredients is prioritized based on frequency of use, concentration used, the area of use, and consumer complaints. The CIR conclusions are available from the CTFA.

In addition to the CIR process the cosmetic industry has instituted a second, important, self-regulatory procedure: the voluntary reporting of adverse reactions, which is intended to provide data on the type and incidence of adverse reactions noted by consumers or by their medical advisors. This reporting procedure creates early awareness of problems handled outside hospital emergency facilities or centers for acute poisoning.

Safety testing of a finished cosmetic product should be sufficient to ensure that the product does not cause irritation when used in accordance with directions, neither elicits sensitization nor includes a sensitizer, and does not cause photoallergic responses. Some of the methods for determining animal or human responses to cosmetics are noted in Table 3.

A particularly critical test for establishing the safety of cosmetics is the exaggerated-use test, in which panelists, often under medical supervision, use a product at frequencies that exceed the normally expected usage. Any adverse reactions, including subjective reports of burning or itching without clinical symptoms, suggest that the product should be examined further. This test also can be used to elicit comments concerning product acceptability.

Repeated usage of certain common cosmetic ingredients can elicit a response within the sebaceous gland apparatus that generates comedos. The cause of this phenomenon is not entirely clear, but an animal (rabbit ear) test purportedly measures the comedogenic potential of cosmetic ingredients or finished products (24). Controversy surrounds the identity of comedogenic substances and the concentration required to elicit the response. Thus use of cosmetic ingredients that have been suspected of causing comedogenicity are generally avoided.

5.2. Production Facilities. The manufacture of acceptable cosmetic products requires not only safe ingredients but also facilities that maintain

Table 3. **Cosmetic Safety Tests**

	Test vehicle	
Determination	Animals	Humans
primary irritation	acute albino rabbit with or without scarification[a]	chronic (21 days) occlusive; chamber scarification[b] Duhring soap chamber[c]
contact allergy	guinea pig maximization (with or without Freund's omplement adjuvant)[d]	repeat patch test (open and closed); maximization test[e]
phototoxicity	hairless mouse and other species plus uvA irradiation[f]	human test[f,g]
photoallergy	guinea pig plus uvA/uvB irradiation[h]	photomaximization test[i]
eye irritation	Draize rabbit eye test[j]	eye instillation using diluted product
comedogenicity	rabbit ear[k]	in-use test
sting test		face[l,m]

[a] Ref. 11. [b] Ref. 12. [c] Ref. 13. [d] Ref. 14. [e] Ref. 15. [f] Ref. 16. [g] Ref. 17.
[h] Ref. 18. [i] Ref. 19. [j] Ref. 20. [k] Ref. 21. [l] Ref. 22. [m] Ref. 23.

high standards of quality and cleanliness. Most countries have established regulations intended to assure that no substandard product or batch is distributed to consumers. Good Manufacturing Practices (GMP) represent workable standards that cover every aspect of drug manufacture, from building construction to distribution of finished products. GMPs in the United States that have been established for drug manufacture are commonly used in cosmetic production (6,25).

5.3. Contamination. Manufacturers of cosmetics must be careful to guard against chemical and microbial contamination. Chemical contamination, which may result from the presence of undesirable impurities in raw materials, is avoidable by adhering to rigid specifications for raw materials. Compendial specifications and publications by the CTFA and other professional societies form the basis of most intracompany raw material specifications. Moreover, all packaging components must meet not only physical and design specifications but also such chemical requirements as extractables and absence of dust and similar contaminants (see PACKAGING, COSMETICS AND PHARMACEUTICALS).

Chemical contamination arising from overheating or other decomposition reactions during processing or from improper storage of incoming supplies must also be avoided. For these reasons, adherence to documented production processes and periodic reassays of stored supplies are required. Additionally, final chemical or physical examinations of the finished and filled products are required to ascertain that no inadvertent chemical contamination has occurred during manufacture and that no undesirable ingredients are present.

An entirely different type of contamination arises from the presence of microbiota in a product. As in the case of chemical contamination, compendial requirements for microbiological purity exists. Pharmacopoeial standards vary from country to country, and manufacturers must use the specifications and kill times that meet local requirements. As of this writing, the criteria in the

British Pharmacopoeia are more stringent than those established by the CTFA, which are stricter than those in the *United States Pharmacopoeia*. In order to meet commonly accepted standards of microbial purity, manufacturing facilities must be periodically cleaned and all products that can support microbial growth must contain an effective preservative (6).

5.4. Stability. An additional mandatory requirement for cosmetic products is chemical and physical stability. Interactions between ingredients that lead to new chemical entities or decomposition products are unacceptable. Stability testing becomes particularly critical if the product includes an active or drug constituent for which a specific performance claim is made. In the absence of an expiration date, a cosmetic product or an OTC drug should be stable for 60 months at ambient temperature. This temperature is a function of climatic zones. Therefore, controlled temperature storage, sometimes at controlled relative humidity, is universally recognized as ideal despite its attendant cost. In order to demonstrate long-term chemical stability on the basis of short- or intermediate-term studies, formulations are stored routinely at elevated temperatures, normally 37, 45, or 50°C. Changes are extrapolated to ambient temperatures using the Arrhenius equation for reaction rates.

Another type of chemical change is initiated by light, which may trigger autolytic, that is, free radical (Type I) or singlet oxygen (Type II) reactions. These changes are routinely classified as oxidation. Rancidity in cosmetics, especially those containing unsaturated lipids, is commonly prevented by use of antioxidants (qv).

Requirements for physical stability in cosmetics are not as rigid as those for chemical stability. As a rule, minor changes in viscosity or appearance are acceptable to users. More drastic changes, resulting from separation of an emulsion because of creaming or oiling, are not acceptable. Short-term physical, or viscosity, changes cannot be extrapolated to long-term performance. Changes observed during static viscosity tests have little predictive value for long-term viscosity or emulsion stability. Short-term dynamic viscosity tests also do not allow prediction of long-term viscosity changes, but these can sometimes be used to predict changes in the nature of emulsions. Zeta potential and particle size determination can provide predictive information on emulsion behavior.

5.5. Performance. Consumer acceptance is a criterion on which cosmetic marketers cannot compromise. Whereas the likes and dislikes of consumers are in a state of constant flux, some product features are critical. A deodorant that does not deodorize or a hair coloring that fades in sunlight is unacceptable. Performance is tested by *in vitro* techniques during formulation, but the ultimate test of a product's performance requires in-use experience with consumers and critical assessment by trained observers. Performance tests can sometimes be combined with in-use safety tests, and protocols for such programs have been developed.

6. Ingredients

Manufacturers of cosmetics employ a surprisingly large number of raw materials. Some of these ingredients are active constituents that have purported beneficial effects on the skin, hair, or nails, for example, acting as moisturizers or conditioners. These substances are generally used in limited quantities. Other ingredients are used to formulate or create the vehicle. These are bulk chemicals used in comparatively large amounts. The resulting combination of various substances affects the nature (viscosity, oiliness, etc) of the finished cosmetic. As a rule numerous combinations and permutations are tested to optimize textural characteristics and to match these to consumers' preferences. Finally, cosmetics may include substances added primarily to appeal to consumers. These ingredients need not contribute appreciably to product performance.

About 6000 different cosmetic ingredients have been identified (7). These can be divided into smaller groups according to chemical similarity or functionality. Table 4 represents a breakdown by functionality on the skin or in the product. The chemical identity of only one ingredient that performs the desired function is given. In most cases, other equally effective substances exist. The diversity of functions required in cosmetics is evident, and cosmetic ingredients may perform more than one function or belong to more than one chemical class. A typical example is sodium DL-2-pyrrolidinone-5-carboxylate (sodium PCA) [28874-51-3], $NaC_5H_7NO_3$. Chemically, this compound may be viewed as an amide, a heterocyclic compound, or an organic salt; functionally, it is a humectant and skin-conditioning agent.

Ingredients exhibiting certain functions are required in many types of cosmetic products. Antioxidants and preservatives are especially critical for product shelf life and quality during usage. Shelf life is defined herein as that period of time during which a product in an unopened package maintains its quality and performance and shows no physical or chemical instability. Antioxidants and preservatives do not contribute to physical stability but are included in cosmetic products to ensure oxidative stability and to control microbial contamination. Once a package has been opened, oxidative processes may cause the product to deteriorate, and microbial species may gain access to the product. These additives are expected to impart some protection even under these circumstances.

6.1. Antioxidants.

Some antioxidants useful in cosmetics are listed in Table 5. The operant mechanisms are interference with radical propagation reactions, reaction with oxygen, or reduction of active oxygen species. Antioxidants are intended to protect the product but not the skin against oxidative damage resulting from ultraviolet radiation or singlet oxygen formation.

6.2. Preservatives.

Several microorganisms can survive and propagate on unpreserved cosmetic products. Preservatives are routinely added to all preparations that can support microbial growth. The choice of a preservative for a given product is difficult. Anhydrous preparations and products containing high levels of ethanol or *i*-propanol may not require the addition of preservatives.

Contamination during manufacture is common, even when microbially clean ingredients are used. Water, which is almost ubiquitous in cosmetic products, is especially troublesome and must be free from contaminating microorganisms. All other ingredients should be screened for the presence of microbial species and batches of raw materials of dubious purity may have to be rejected. Cleanliness during manufacture, processing, and filling must be strictly maintained. Despite these precautions, microbial integrity of products may require the presence of one or more preservatives that are compatible with the product's

Table 4. **Cosmetic Functions and Representative Ingredients**[a]

Function	Ingredient[b]	Molecular formula	CAS Registry number
Biologically active agents			
antiacne	salicylic acid	$C_7H_6O_3$	[69-72-7]
anticaries	monosodium fluorophosphate	Na_2HPO_3F	[10163-15-2]
antidandruff	zinc pyrithione	$C_{10}H_8N_2O_2S_2Zn$	[13463-41-7]
antimicrobial	benzalkonium chloride		[8001-54-5]
antiperspirant	aluminum chlorohydrate	$Al_2ClH_5O_5$	[12042-91-0]
biocides	triclosan	$C_{12}H_7Cl_3O_2$	[3380-34-5]
sunscreen	octyl methoxycinnamate	$C_{18}H_{26}O_3$	[5466-77-3]
skin protectant	dimethicone	$(C_2H_6OSi)_nC_4H_{12}Si$	[9006-65-9]
			[63148-62-9]
		$(C_2H_6OSi)_n$	[9016-00-6]
external analgesic	methyl salicylate	$C_8H_8O_3$	[119-36-8]
Nonbiologically active agents			
abrasive			
skin	oatmeal		
teeth	dicalcium phosphate	$Ca_2(HPO_4)_2$	[7757-93-9]
antifoam	simethicone		[8050-81-5]
antioxidant	ascorbic acid	$C_6H_8O_6$	[50-81-7]
antistatic agent	dimethylditallow alkylammonium chlorides		[68783-78-8]
binder	hydroxypropylcellulose		[9004-64-2]
chelator	hydroxyethyl ethylenediamine triacetic acid (HEDTA)	$C_{10}H_{18}N_2O_7$	[150-39-0]
colorant			
pigment	ultramarine	$Na_7Al_6Si_6O_{24}S_2$	[1317-97-11]; [1345-00-2]; [12769-96-9]
dye	FD&C Red No. 4	$C_{18}H_{16}N_2O_7S_2 \cdot 2Na$	[4548-53-2]
emulsion stabilizer	xanthan gum		[11138-66-2]
film former	PVP	$(C_6H_9NO)_x$	[9003-39-8]
hair colorant	*p*-phenylenediamine	$C_6H_8N_2$	[106-50-3]
hair conditioner	sodium lauroamphoacetate	$Na_2C_{18}H_{35}N_2O_3 \cdot HO$	[14350-96-0]
humectant	glycerol	$C_3H_8O_3$	[56-81-5]
deodorant			
mouth	zinc chloride	$ZnCl_2$	[7646-85-7]
external	cetylpyridinium chloride	$C_{21}H_{38}ClN$	[123-03-5]
preservative	propylparaben	$C_{10}H_{12}O_3$	[94-13-3]
emollient	octyl stearate	$C_{26}H_{52}O_2$	[22047-49-0]
skin-conditioning agent			
general	pyrrolidinone carboxylic acid (PCA)	$C_5H_7NO_3$	[98-79-3]
occlusive	petrolatum	C_nH_{2n+2}	[8009-03-8]
film forming	hyaluronic acid		[9004-61-9]
solvent	ethanol	C_2H_6O	[64-17-5]
cleansing agent	sodium lauryl sulfate	$C_{12}H_{25}NaO_4S$	[151-21-3]
emulsifying agent	polysorbate 65		[9005-71-4]
foam booster	cocamide DEA		[68140-00-1]
suspending agent	sodium lignosulfonate		[8061-51-6]
hydrotrope	sodium toluenesulfonate		[12068-03-0]
viscosity-controlling agent			
decrease	propylene glycol	$C_3H_8O_2$	[57-55-6]
increase	hydroxypropylmethylcellulose		[9004-65-3]

[a] Additional functions may be found in Ref. 26.

[b] CTFA adopted names are used; this notation is used for cosmetic labeling.

Table 5. **Free-Radical-Inhibiting Antioxidants or Reductants Useful in Cosmetics**[a,b]

Antioxidant	CAS Registry number	Molecular formula
ascorbic acid	[50-81-7]	$C_6H_8O_6$
ascorbyl palmitate	[137-66-6]	$C_{22}H_{38}O_7$
butylated hydroxyanisole (BHA)	[25013-16-5]	$C_{11}H_{16}O_2$
butylated hydroxytoluene (BHT)	[128-37-0]	$C_{15}H_{24}O$
t-butyl hydroquinone	[1948-33-0]	$C_{10}H_{14}O_2$
cysteine	[52-90-4]	$C_3H_7NO_2S$
dilauryl thiodipropionate	[123-28-4]	$C_{30}H_{58}O_4S$
dodecyl gallate	[1166-52-5]	$C_{19}H_{30}O_5$
ellagic acid	[476-66-4]	$C_{14}H_6O_8$
erythorbic acid	[98-65-6]	$C_6H_8O_6$
kaempferol	[520-18-3]	$C_{15}H_{10}O_6$
nordihydroguaiaretic acid	[500-38-9]	$C_{18}H_{22}O_4$
propyl gallate	[121-79-9]	$C_{10}H_{12}O_5$
quercetin	[117-39-5]	$C_{15}H_{10}O_7$
sodium ascorbate	[134-03-2]	$C_6H_7NaO_6$
sodium sulfite	[7757-83-7]	Na_2SO_3
thioglycolic acid	[68-11-1]	$C_2H_4O_2S$
tocopherol	[59-02-9]; [1406-18-4]	$C_{28}H_{48}O_2$

[a] Ref. 26 includes a more comprehensive listing.

[b] Use levels are normally about 0.1% and rarely exceed 0.2%.

ingredients. Products should not support the growth or viability of any microbial species that may have been accidentally introduced. Preservatives are also required to reduce contamination by consumers during normal use. Powerful preservative action to create self-sterilizing products is required. Whereas production of sterile cosmetics may be practicable, maintenance of sterility during use is problematical, because fingers and cosmetic applicators are not sterile.

Pharmacopoeias and CTFA publications provide guidelines for challenge test procedures and limits on microbial counts (25). The compendial requirements for kill of microorganisms vary significantly, and alternative test methods may be required (27). As a general rule, pathogenic organisms should be absent (28). Table 6 lists a number of antimicrobial preservatives used in cosmetic products. Experience has shown that some of the most commonly used preservatives are inactivated by a variety of surfactants. For example, the parabens (esters of *p*-hydroxybenzoic acid) are exceptionally sensitive to the presence of nonionic surfactants, presumably as a result of micellization of the antimicrobial by the surfactant. Over the years, preservation problems have resulted in the introduction into cosmetics of unusual substances that exhibit suitable antimicrobial spectra. However, some of these ingredients reportedly are irritants or sensitizers. Controversies in the scientific literature over the use of these substances are aggravated by regulatory acceptance or prohibition, which may differ from country to country. Table 6 includes preservatives that may be barred in certain countries.

Local restrictions concerning the inclusion of preservatives and other constituents are dependent on the cosmetic product's method of use. Products that are allowed to remain on the skin are differentiated from those that are meant to

Table 6. **Antimicrobial Preservatives Useful in Cosmetics**[a,b]

Name	CAS Registry number	Molecular formula
benzoic acid[c]	[65-85-0]	$C_7H_6O_2$
benzyl alcohol	[100-51-6]	C_7H_8O
5-bromo-5-nitro-1,3-dioxane	[30007-47-7]	$C_4H_6BrNO_4$
2-bromo-2-nitropropane-1,3-diol	[52-51-7]	$C_3H_6BrNO_4$
butylparaben	[94-26-8]	$C_{11}H_{14}O_3$
calcium propionate	[4075-81-4]	$CaC_6H_{10}O_4$
chlorobutanol	[57-15-8]	$C_4H_7Cl_3O$
m-cresol	[108-39-4]	C_7H_8O
o-cresol	[95-48-7]	C_7H_8O
p-cresol	[106-44-5]	C_7H_8O
DEDM hydantoin	[26850-24-8]	$C_9H_{16}N_2O_4$
dehydroacetic acid	[520-45-6]	$C_8H_8O_4$
diazolidinyl urea	[278-92-2]	$C_{11}H_8O_2$
dimethyl oxazolidine	[51200-87-4]	$C_5H_{11}NO$
DMDM hydantoin	[6440-58-0]	$C_7H_{12}N_2O_4$
7-ethylbicyclooxazolidine	[7747-35-5]	$C_7H_{13}NO_2$
ethylparaben	[120-47-8]	$C_9H_{10}O_3$
formaldehyde	[50-00-0]	CH_2O
glutaral	[111-30-8]	$C_5H_8O_2$
glyoxal	[107-22-2]	$C_2H_2O_2$
imidazolidinyl urea	[39236-46-9]	$C_{11}H_{16}N_8O_8$
iodopropynyl butylcarbamate	[55406-53-6]	$C_8H_{12}INO_2$
isobutylparaben	[4247-02-3]	$C_{11}H_{14}O_3$
isopropylparaben	[4191-73-5]	$C_{10}H_{12}O_3$
MDM hydantoin	[116-25-6]	$C_6H_{10}N_2O_3$
methylchloroisothiazolinone	[26172-55-4]	C_4H_4ClNOS
methyldibromoglutaronitrile	[35691-65-7]	$C_6H_6Br_2N_2$
methylisothiazolinone	[2682-20-4]	C_4H_5NOS
methylparaben	[99-76-3]	$C_8H_8O_3$
phenethyl alcohol	[200-456-2]	$C_8H_{10}O$
phenol	[108-95-2]	C_6H_6O
phenoxyethanol	[122-99-6]	$C_8H_{10}O_2$
phenylmercuric acetate	[62-38-4]	$HgC_8H_8O_2$
phenylmercuric benzoate	[94-43-9]	$HgC_{13}H_{10}O_2$
phenylmercuric borate	[102-98-7]	$HgC_6H_7BO_3$
o-phenylphenol	[90-43-7]	$C_{12}H_{10}O$
propylparaben	[94-13-3]	$C_{10}H_{12}O_3$
Quaternium-14	[27479-28-3]	$C_{23}H_{42}N \cdot Cl$
Quaternium-15	[51229-78-8]	$C_9H_{16}ClN_4 \cdot Cl$
sodium dehydroacetate	[4418-26-2]	$NaC_8H_7O_4$
sodium phenolsulfonate	[1300-51-2]	$NaC_6H_5O_4S$
sodium phenoxide	[139-02-6]	NaC_6H_5O
sodium pyrithione	[3811-73-2]	NaC_5H_5NOS
sorbic acid[c]	[110-44-1]	$C_6H_8O_2$
thimerosal	[54-64-8]	$NaHgC_9H_9O_3S$
triclocarban	[101-20-2]	$C_{13}H_9Cl_3N_2O$
triclosan	[3380-34-5]	$C_{12}H_7Cl_3O_2$
zinc pyrithione	[13463-41-7]	$ZnC_{10}H_8N_2O_2S_2$

[a] Ref. 26 includes a more comprehensive listing.

[b] Use levels are product dependent but generally do not exceed 0.25%.

[c] The acid salts are also used.

be rinsed off. Components of products left on the skin can be expected to penetrate the viable epidermis and to be systematically absorbed. Products that are rinsed off shortly after skin contact, such as shampoos, can, if properly labeled, contain preservatives that might elicit adverse reactions if left on the skin. Typical examples of such preservatives are formaldehyde, formaldehyde releasers such as Quaternium 15 or MDM hydantoin, and the blend of methylchloroisothiazolinone and methylisothiazolinone.

Decorative eye cosmetic products have been reported to be subject to pathogenic microbial contamination. Regulatory agencies in several countries, therefore, permit the use of mercury-containing preservatives in eye makeups. The infections reported were to a large extent caused by contamination during use, and the introduction of self-sterilizing preparations seems warranted.

6.3. Lipids. Natural and synthetic lipids are used in almost all cosmetic products. Lipids serve as emollients or occlusive agents, lubricants, binders for creating compressed powders, adhesives to hold makeup in place, and hardeners in such products as lipsticks. In addition, lipids are used as gloss-imparting agents in hair-care products. The primary requirements for lipids in cosmetics are absence of excessive greasiness and ease of spreading on skin. Oily lipids, principal constituents of emulsions (creams and lotions), are well suited for inclusion in massage products, oils used to treat the skin (bath oils), ointments, suntan oils, and the like. Selection for a specific application is made on the basis of chemical inertness and physical properties. Petrolatum, mineral oils, polymeric silicones, polybutenes, and related substances are ingredients used for skin and hair conditioning. Conditioning is cosmetic jargon for describing a substance's beneficial effect on the substrate. For example, quaternary compounds are substantive to skin and hair proteins and thus can produce conditioning effects. Similarly, lipidic compounds without substantive functional groups, for example, tricaprin, condition skin merely by their presence on the surface. A selected listing of cosmetically useful lipids is provided in Table 7.

6.4. Solvents. Solvents can be added to cosmetics to help dissolve components used in cosmetic preparations. Water is the most common solvent and is the continuous phase in most suspensions and water/oil (w/o) emulsions. Organic solvents are required in the preparation of colognes, hair fixatives, and nail lacquers. Selected solvents are used to remove soil, sebum, and makeup from skin. Solvents used in cosmetics include acetone, denatured alcohol, butoxyethanol (ethyleneglycol monobutylether), diethylene glycol, dimethyl isosorbide, ethyl acetate, heptane, isopropyl alcohol, mineral spirits (boiling range 110–155°C), polyethylene glycol (mol wt from 200 up to 15,000), propylene glycol, toluene, and tricaprin (glyceryl tri-*n*-decanoate). A comprehensive listing may be found in Reference 26. The selection of solvents for use in cosmetics is a complex task because of odor as well as topical and inhalation toxicities.

6.5. Surfactants. Substances commonly classified as surfactants (qv) or surface active agents are required in a wide variety of cosmetics. These are often categorized on the basis of ionic character but are grouped in Table 8, which includes at least one member from each of the various chemical types of surfactants, on the basis of utility in cosmetics. Prolonged contact with anionic surfactants can cause some swelling of the skin. Although this is a temporary phenomenon, skin in this swollen condition allows permeation of externally

Table 7. **Cosmetically Useful Lipids**[a]

Material	CAS Registry number	Molecular formula
	Emollients	
butyl oleate	[142-77-8]	$C_{22}H_{42}O_2$
caprylic/capric glycerides	[65381-09-1]	
cetyl lactate	[35274-05-6]	$C_{19}H_{38}O_3$
dibutyl sebacate	[109-43-3]	$C_{18}H_{34}O_4$
diisobutyl adipate	[141-04-8]	$C_{14}H_{26}O_4$
ethyl linoleate	[544-35-4]	$C_{20}H_{26}O_2$
glyceryl isostearate	[32057-14-0]	$C_{21}H_{42}O_4$
hydrogenated palm kernel glycerides[b]		
isodecyl myristate	[17670-91-6]	$C_{24}H_{48}O_2$
isopropyl stearate	[112-10-7]	$C_{21}H_{42}O_2$
lauryl lactate	[6283-92-7]	$C_{15}H_{30}O_3$
mineral oil	[8012-95-1]	C_nH_{2n}
myristyl myristate	[3234-85-3]	$C_{24}H_{56}O_2$
oleyl oleate	[3687-45-4]	$C_{36}H_{68}O_2$
PPG-10 cetyl ether	[9035-85-2]	$(C_3H_3O)_2C_{16}H_{34}O$
propylene glycol dicaprylate	[7384-97-6]	$C_{15}H_{19}NOS \cdot HCl$
squalene	[111-02-4]	$C_{30}H_{50}$
wheat germ glycerides	[58990-07-8]	
	Occlusive agents	
acetylated lanolin	[61788-48-5]	
butyl stearate	[123-95-5]	$C_{22}H_{44}O_2$
caprylic/capric triglyceride	[65381-09-1]	
dimethicone	[9006-65-9]	$(C_2H_6OSi)_nC_4H_{12}Si$
hydrogenated rice bran wax[c]		
lauryl stearate	[5303-25-3]	$C_{30}H_{60}O_2$
paraffin	[8002-74-2]	C_nH_{2n+2}
pentarerythritol tetrastearate	[115-83-3]	$C_{77}H_{148}O_8$
petrolatum	[8009-03-8]	C_nH_{2n+2}
propylene glycol dipelargonate	[225-350-9]	$C_{21}H_{40}O_4$
stearyl erucate[d]		$C_{40}H_{78}O_2$
trilinolein	[537-40-6]	$C_{57}H_{98}O_6$
	Natural lipids	
apricot kernel oil	[72869-69-3]	
beeswax	[8006-40-4]	
carnauba	[8015-86-9]	
castor oil	[8001-79-4]	
coconut oil	[8001-31-8]	
japan wax	[8001-39-6]	
jojoba wax	[66625-78-3]	
lanolin	[8006-54-0]	
mink oil[e]		
olive oil	[8001-25-0]	
ozokerite	[8021-55-4]	
rice bran oil	[68553-81-1]; [84696-37-7]	
sesame oil	[8008-74-0]	
sunflower seed oil	[8001-21-6]	
vegetable oil	[68956-68-3]	
walnut oil	[8024-09-7]	

[a] Ref. 26 includes a more comprehensive listing.

[b] This is a hydrogenated mixture of mono-, di-, and triglycerides derived from palm kernel oil.

[c] Prepared by partial hydrogenation of rice bran wax.

[d] Erucic acid, *n*-octadecanol ester.

[e] Oil obtained from subdermal fatty tissue of genus *Mustela*.

Table 8. **Cosmetic Surfactants**[a]

Material[b]	CAS Registry number	Molecular formula
Cleansing agents		
ammonium laureth sulfate[c,d]	[32612-48-9]	$(C_2H_4O)_nC_{12}H_{26}O_4S \cdot H_3N$
cetalkonium chloride	[122-18-9]	$C_{25}H_{46}N \cdot Cl$
DEA myristate	[53404-39-0]	$C_{14}H_{28}O_2 \cdot C_4H_{11}NO_2$
decyl polyglucose[d,e]		
dioctyl sodium sulfosuccinate[c,d]	[577-11-7]	$C_{20}H_{38}O_7S \cdot Na$
disodium cocoamphodiacetate[d]	[68650-39-5]	
disodium laurimino dipropionate[d]	[3655-00-3]	$C_{18}H_{35}NO_4 \cdot 2Na$
lauryl betaine[c,d]	[683-10-3]	$C_{16}H_{33}NO_2$
lauryl pyrrolidone[d]	[2687-96-9]	$C_{16}H_{31}NO$
nonoxynol-12	[9016-45-9]	$(C_2H_4O)_nC_{15}H_{24}O$
myristamine oxide[c,d]	[3332-27-2]	$C_{16}H_{35}NO$
PEG-50 stearate	[9004-99-3]	$(C_2H_4O)_nC_{18}H_{36}O_2$
potassium dodecylbenzenesulfonate[d]	[27177-77-1]	$KC_{18}H_{30}O_3S$
potassium oleate	[143-18-0]	$KC_{18}H_{34}O_2$
sodium cocoyl glutamate[d]	[68187-32-6]	
sodium C_{14-16} olefin sulfonate[d]	[68439-57-6]	
sodium laureth phosphate[c,d]	[42612-52-2]	
sodium lauryl sulfate[c,d]	[151-21-3]	$NaC_{12}H_{26}O_4S$
sodium methyl oleoyl taurate[c]	[137-20-2]	$NaC_{21}H_{41}NO_4S$
sodium nonoxynol-25 sulfate	[9014-90-8]	$(C_2H_4O)_nC_{15}H_{24}O_4S \cdot Na$
sodium oleoyl isethionate[d]	[142-15-4]	$NaC_{20}H_{38}O_5S$
sodium stearate[c]	[822-16-2]	$NaC_{18}H_{36}O_2$
TEA-abietoyl hydrolyzed collagen[d]	[68918-77-4]	
TEA-lauryl sulfate[d]	[139-96-8]	$C_{12}H_{26}O_4S \cdot C_6H_{15}NO_3$
TEA-oleoyl sarcosinate[c]	[17736-08-2]	$C_{21}H_{39}NO_3 \cdot C_6H_{15}NO_3$
Emulsifying agents		
ceteareth-10	[68439-49-6]	
cetrimonium bromide	[57-09-0]	$C_{19}H_{42}N \cdot Br$
laneth-5	[3055-95-6]	$C_{22}H_{46}O_6$
lecithin	[8002-43-5]	
nonoxynol-9	[14409-72-4]	$C_{33}H_{60}O_{10}$
PEG-20 dilaurate	[9005-02-1]	$(C_2H_4O)_nC_{24}H_{46}O_3$
PEG-8 oleate	[9004-96-0]	$(C_2H_4O)_nC_{18}H_{34}O_2$
poloxamer 407	[9003-11-6]	$(C_3H_6O \cdot C_2H_4O)_x$
polyglyceryl-8 oleate	[9007-48-1]	
polysorbate 60	[9005-67-8]	
sorbitan sequioleate	[8007-43-0]	
sucrose stearate	[25168-73-4]	$C_{30}H_{56}O_{12}$
Foam boosters		
cocamine oxide	[61788-90-7]	
lauramide DEA	[120-40-1]	$C_{16}H_{33}NO_3$
myristamide MIPA	[10525-14-1]	$C_{17}H_{35}NO_2$
myristaminopropionic acid	[14960-08-8]	$C_{17}H_{35}NO_2$
Hydrotropes		
ammonium xylenesulfonate	[26447-10-9]	$C_8H_{10}O_3S \cdot H_3N$
potassium toluenesulfonate	[16106-44-8]	$C_7H_8O_3S \cdot K$
sodium methyl naphthalene sulfonate	[26264-58-4]	$C_{11}H_{10}O_3S \cdot Na$
Solubilizing agents		
cetareth-40	[68439-49-6]	
oleth-44	[9004-98-2]	$(C_2H_4O)_nC_{18}H_{36}O$
PEG-40 stearate	[9004-99-3]	$(C_2H_4O)_2C_{18}H_{36}O_2$

Table 8 (*Continued*)

Material[b]	CAS Registry number	Molecular formula
	Suspending agents	
behentrimonium chloride	[17301-53-0]	$C_{25}H_{54}N \cdot Cl$
benzethonium chloride	[121-54-0]	$C_{27}H_{42}NO_2 \cdot Cl$
sodium lignosulfonate	[8061-51-6]	
sodium polystyrene sulfonate	[9003-59-2]	$(C_8H_8O_3S \cdot Na)_x$

[a] Ref. 26 includes a comprehensive listing.

[b] CFTA names are used.

[c] Belongs to a chemical class especially useful in facial and body washes.

[d] Belongs to a chemical class especially useful in shampoos.

[e] Decylether of a glucose oligomer.

applied substances. Nonionic surfactants as a group are generally believed to be mild even under exaggerated conditions. The more hydrophobic nonionics, those that are water dispersible (not water-soluble), can enhance transdermal passage. Amphoteric surfactants as a group exhibit a favorable safety profile. Finally, cationic surfactants are commonly rated as more irritating than the anionics, but the evidence for generalized conclusions is insufficient.

6.6. Colorants. Color (qv) is used in cosmetic products for several reasons: the addition of color to a product makes it more attractive and enhances consumer acceptance; tinting helps hide discoloration resulting from use of a particular ingredient or from age; and finally, decorative cosmetics owe their existence to color.

Organic Colorants. The importance of coal-tar colorants cannot be overemphasized. The cosmetic industry, in cooperation with the FDA, has spent a great deal of time and money in efforts to establish the safety of these dyes (see COLORANTS FOR FOOD, DRUGS, COSMETICS, AND MEDICAL DEVICES). Contamination, especially by heavy metals, and other impurities arising from the synthesis of permitted dyes are strictly controlled. Despite this effort, the number of usable organic dyes and of pigments derived from them has been drastically curtailed by regulatory action.

In addition to the U.S. certified coal-tar colorants, some noncertified naturally occurring plant and animal colorants, such as alkanet, annatto [1393-63-1], carotene [36-88-4], $C_{40}H_{56}$, chlorophyll [1406-65-1], cochineal [1260-17-9], saffron [138-55-6], and henna [83-72-7], can be used in cosmetics. In the United States, however, natural food colors, such as beet extract or powder, turmeric, and saffron, are not allowed as cosmetic colorants.

The terms FD&C, D&C, and External D&C (Ext. D&C), which are part of the name of colorants, reflect the FDA's colorant certification. FD&C dyes may be used for foods, drugs, and cosmetics; D&C dyes are allowed in drugs and cosmetics; and Ext. D&C dyes are permitted only in topical products. Straight colorants include both the organic dyes and corresponding lakes, made by extending the colorant on a substrate such as aluminum hydroxide or barium sulfate. The pure dye content of these lakes varies from 2 to 80%; the organic dyes contain over 80% pure dye. Colorants certified for cosmetic use may not contain more

Table 9. **Inorganic Pigments Useful in Makeups**

Material	Molecular formula	Color
titanium dioxide	TiO_2	white
zinc oxide	ZnO	white
talc	steatite	whitish
barium sulfate	$BaSO_4$	white
mica		glossy, colorless
titanium dioxide–ferric oxide coated mica	[a]	glossy, nacreous, multicolored
		multicolored
guanine[b]	$C_5H_5N_5O$	nacreous
bismuth oxychloride	BiOCl	white, nacreous
iron oxides	85% Fe_2O_3	yellow to orange
umber	Fe_2O_3/Fe_3O_4	brown
sienna	Fe_2O_3 (ignited)	red
	Fe_3O_4	black
chrome hydroxide green	$Cr_2O(OH)_4$	bluish green
chrome oxide greens	Cr_2O_3	green
ferric ammonium ferrocyanide	$Fe(NH_4)[Fe(CN)_6]$	blue
ferric ferrocyanide	$Fe_4[Fe(CN)_6]_3$	blue
manganese violet	$Mn(NH_4)P_2O_7$	violet
ultramarines[c]		blue, violet, red, pink, green

[a] Material is a mixture.

[b] Guanine [73-40-5], an organic dye, is also known as CI 75170 [73-40-5].

[c] Materials are fusion mixtures.

than 0.002% of lead, not more than 0.0002% of arsenic, and not more than 0.003% of heavy metals other than lead and arsenic.

Inorganic Colorants. In addition to various white pigments, other inorganic colorants such as those listed in Table 9 are used in a number of cosmetic products. These usually exhibit excellent lightfastness and are completely insoluble in solvents and water.

Naturally occurring colored minerals that contain oxides of iron are known by such names as ochre [1309-37-1], umber [12713-03-0], sienna [1309-37-1], etc. These show greater variation in color and tinting power than the synthetic equivalents, and the nature and amount of impurities in the national products is also variable. Most of the pigments identified in Table 9 are, therefore, manufactured synthetically. They are primarily used in skin-makeup products and in eye-area colorants.

Nacreous Pigments. For many years nacreous pigments were limited to guanine (from fish scales) and bismuth oxychloride. Mica, gold, copper, and silver, in flake form, can also provide some interesting glossy effects in products and on the face. Guanine is relatively costly, and bismuth oxychloride darkens on exposure to light and is difficult to suspend because of its high specific gravity. An entirely new set of colored, iridescent, inorganic pigments, which may be described as mixtures of mica and titanium dioxide (sometimes with iron oxides), has been created by coating mica flakes with titanium dioxide. The wavelengths of light reflected from these compositions can produce a complete range of colored interference patterns. The particle size of the mica must be controlled and may not exceed 150 μm, at least in the United States. Additional color effects can be created by sandwiching the mica, TiO_2, and Fe_2O_3.

7. Specialized Cosmetic Technologies

Several specialized technologies have been perfected for cosmetic products. Among these, emulsification, stick technology, and powder blending are prominent.

8. Emulsification

Emulsification is essential for the development of all types of skin- and hair-care preparations and a variety of makeup products. Emulsions (qv) are fine dispersions of one liquid or semisolid in a second liquid (the continuous phase) with which the first substance is not miscible. Generally, one of the phases is water and the other phase is an oily substance: oil-in-water emulsions are identified as o/w; water-in-oil emulsions as w/o. When oil and water are mixed by shaking or stirring in the absence of a surface-active agent, the two phases separate rapidly to minimize the interfacial energy. Maintenance of the dispersion of small droplets of the internal phase, a requirement for emulsification, is practical only by including at least one surface-active emulsifier in the oil-and-water blend.

The addition of emulsifiers (see Table 8) lowers the energy of the large interfacial area created by forming a huge number of small droplets from a single large drop. In practical emulsification technology, this thermodynamic emulsion stabilization is augmented by two other features. One is the formation of a rigid interfacial film on the surface of the droplets of the internal phase (29). This film, sometimes exhibiting the optical characteristics of a liquid crystal, acts as a mechanical barrier to the coalescence of the droplets of the internal phase. Finally, the droplets may be stabilized by the formation of an electric double layer, which favors the electrical repulsion between charged particles. The latter requires the presence of an electrolyte or an ionized emulsifier.

The coalescence of internal phase droplets can be further decreased by raising the viscosity of the external continuous phase through addition of gums or synthetic polymers, for example, cellulosic gums such as hydroxypropyl methyl-cellulose [9004-65-3], fermentation gums such as xanthan gum [11138-66-2], or cross-linked carboxyvinyl polymers such as carbomer [39007-16-3]. The increased viscosity also counteracts changes in the emulsion resulting from differences in the specific gravity of the two phases as mandated by Stokes' law. An advance in cosmetic emulsification technology has resulted from the development of cross-linked carboxyvinyl polymers, in which some of the carboxylic acid residues are esterified with various fatty alcohols. These polymers possess the ability to act as primary emulsifiers and thicken the system when some of the remaining carboxylic groups are neutralized with alkali (see CARBOXYLIC ACIDS).

The selection of emulsifiers, auxiliary emulsifiers, gums, and other components is complicated and largely empirical. Despite the lack of a rigid theoretical basis, the hydrophile/lipophile balance (HLB) is the most useful approach for the selection of nonionic emulsifiers (30). The inclusion of ionic emulsifiers was not contemplated in the original formulation of the HLB system. The HLB system also does not account for the effect of low HLB viscosity increasing ingredients, such as cetyl alcohol or glyceryl monostearate. The precise selection of the desired blend from commercial nonionics for emulsification is often frustrating (31). Methods for selecting suitable blends of emulsifiers and stabilizers (32,33), for preparing emulsions (34,35), and for studying stability (36) have been published. The technical literature also includes publications dealing with the theory of emulsification and the structure of emulsions and of microemulsions (37,38).

Conventional cosmetic emulsions (macroemulsions) normally contain about 70% or more of the external phase, which may be a mixture of components. The internal phase is routinely introduced into the external phase at an elevated temperature with vigorous agitation. The emulsifiers are distributed according to their solubility between the two phases. The level of emulsifiers (rarely more than about 10%) is kept low since excessive amounts may destabilize emulsions or form a clear solubilizate. Auxiliary emulsifiers and other components are included in the phases in which they are soluble.

The term multiple emulsion describes a w/o emulsion in an o/w emulsion. For example, when a w/o emulsion is added to water, no dispersion is expected unless the aqueous phase is fortified with a suitable emulsifier. The resulting dispersion may then be a blend of a w/o and an o/w emulsion, or it may be a multiple emulsion of the w/o/w type. In this latter case, the initial w/o emulsion becomes the internal phase of the final product. Generally, these preparations are not very stable unless they are produced under rigidly controlled conditions (32,39,40).

Microemulsions or solubilized or transparent systems are very important in the marketing of cosmetic products to enhance consumer appeal (32,41). As a rule, large quantities of hydrophilic surfactants are required to effect solubilization. Alternatively, a combination of a solvent and a surfactant can provide a practical solution. In modern clear mouthwash preparations, for example, the flavoring oils are solubilized in part by the solvent (alcohol) and in part by the surfactants. The nature of solubilized systems is not clear. Under normal circumstances, microemulsions are stable and form spontaneously. Formation of a microemulsion requires little or no agitation. Microemulsions may become cloudy on heating or cooling, but clarity at intermediate temperatures is restored automatically.

Formation of liposomal vesicles under controlled conditions of emulsification of lipids with phospholipids has achieved prominence in the development of drugs and cosmetics (42). Such vesicles are formed not only by phospholipids but also by certain nonionic emulsifying agents. Formation is further enhanced by use of specialized agitation equipment known as microfluidizers. The almost spontaneous formation of liposomal vesicles arises from the self-assembly concepts of surfactant molecules (43). Vesicles of this type are unusual sustained-release disperse systems that have been widely promoted in the drug and cosmetic industries.

8.1. Stick Technology.

Cosmetic sticks can be divided into three categories: sticks molded in the container; sticks molded separately and then encased; and sticks formed by compression.

Container Molding. Antiperspirant, deodorant, sunscreen, and antiacne sticks are container molded. The amount of dispersed ingredients makes them brittle and difficult to handle mechanically.

The required solids are suspended in a wax–emollient blend at about 60 to 80°C and milled. The liquid suspension is then cooled to about 55°C, and the more volatile ingredients are added. The mass is placed into containers, which are commonly provided with a threaded shaft for raising or lowering the product.

Antiperspirant sticks based on this molding technique have become more popular since volatile low mol wt cyclomethicones [69430-24-6] have been used successfully as the lipids and fatty alcohols as the waxes. This type of product delivers the active antiperspirant to the site as a clinging powder without excessive oiliness.

Deodorant and cologne sticks are formed by allowing sodium stearate to gel in a suitable organic solvent, usually ethanol or propylene glycol. The soap and the solvent are heated under reflux until the soap is dissolved. The solution is cooled to about 60°C; fragrance, color, and the like are added; and the mass is placed into suitable containers.

Stick Molding. Various types of lipsticks and eye-shadow sticks are stick molded. A wax-containing lipid mass is milled with the pigment at elevated (about 75°C) temperatures until it is uniform. The lipid mass, at a temperature about 10°C above its melting point, is then poured into metallic molds. Deaeration is essential to prevent unsightly depressions on the molded sticks. To avoid sudden congealing, the molds are customarily heated to a temperature above room temperature before filling; after filling, they are chilled to temperatures well below room temperature. After unmolding, the sticks may be inserted into various types of containers (swivel, metal, or plastic). In order to formulate acceptable molded sticks, slowly developing surface anomalies or defects must be avoided. Foremost are the excrescence of solid fatty substances (also called bloom) and the exudation of liquid substances (also called sweating). Both of these defects are attributed to polymorphic transformation. The selection of the proper blend of lipids to create an acceptable makeup stick is complex. Some of the lipids used in such products and their primary characteristics are listed in Table 10. Other types of sticks, for example, eyebrow pencils and lip liners, are molded similarly but may be inserted into wooden pencil stock, trimmed, and appropriately finished.

The criteria for a good cosmetic makeup stick are manifold: the sticks must pay off, that is, deliver the desired amount when used at or near room temperature; sticks must withstand exposure to moderately elevated temperatures; they should not break during normal use; stick components must not elicit unpleasant, for example, oily or warming, sensations after application; pigments must be uniformly distributed and must not react photochemically with the remaining stick components to cause rancidity or photoirritation; and finally, the film produced on the body site must be resistant to rubbing off or transferring to eating utensils or clothing.

Compressed-Powder Sticks. Compression of a blend of solids using a suitable binder or by extruding a water containing magma results in compressed-powder sticks.

Table 10. **Lipids Used in Cosmetic Molded Sticks**[a]

Lipid	CAS Registry number	Characteristics
	Oils	
castor oil	[8001-79-4]	high gloss; high viscosity
mineral oil	[8012-95-1]	high gloss
	Esters / Alcohols	
butyl stearate	[123-95-5]	rapid wetting of pigments; controls sweating at elevated temperatures
guerbet alcohols		
decyl tetradecanol	[58670-89-6]	satiny gloss
octyl dodecanol	[5333-42-6]	satiny gloss
isocetyl alcohol	[36311-34-9]	similar to castor oil
isopropyl myristate	[110-27-0]	same as butyl stearate
isopropyl palmitate	[142-91-6]	same as butyl stearate
oleyl alcohol	[143-28-2]	high gloss; turns rancid
	Fats	
cocoa butter	[8002-31-1]	tendency to bloom
glyceryl monostearate	[31566-31-1]	high melting
hydrogenated cocoglycerides[b]		variable properties
hydrogenated vegetable oil	[68334-28-1]	greasy
lanolin	[8006-54-0]	wets pigments
	Waxes	
beeswax	[8006-40-4]	low gloss
candelilla	[8006-44-8]	low melting
carnauba	[8015-86-9]	very hard
ozokerite	[8021-55-4]	thermally stable
	Dye solvents	
ethoxydiglycol acetate	[112-15-2]	bitter
polyethylene glycols	[25322-68-3]	
propylene glycol	[57-55-6]	

[a] Ref. 26 includes comprehensive listings.

[b] These are blends of mono-, di-, and triglycerides of hydrogenated coconut oil.

8.2. Powder Blending. Cosmetic powders serve two primary functions. One group, commonly called body powders or talcs, is applied to the skin to provide lubricity and to absorb excessive moisture. The second group, commonly referred to as face powders, exists in both loose and compressed forms and is used to impart some color to the skin and to dull excessive oiliness.

Most powders, including medicated powders, depend on talc to provide lubricity and a matte finish on the skin. Talc is generally blended with other constituents, such as those listed in Table 11. The plate-like nature of mined talc makes this hydrous magnesium silicate (steatite) an important skin-care constituent. Loose body and makeup powders utilize additional bulk ingredients. The products can also include antimicrobial agents, dyes, and pigments. The selection of a fragrance must be made with great care; some bulk ingredients are alkaline, and the perfume oil on the surface of particles is subject to oxidation, especially if pigmented ingredients are included.

The basic manufacturing process involves thorough blending of the components, especially the pigments, and comminution with the aid of a variety of

Table 11. **Powder Ingredients Used for Cosmetics**

Ingredient	Chemical identity	CAS Registry number	Comment
chalk		[13397-25-6]	opaque, alkaline
kaolin (clay)	aluminum silicate	[1332-58-7]	
	attapulgite	[1337-76-4]	
	fuller's earth	[8031-18-3]	opaque, low gloss
	hectorite	[12173-47-6]	
	montmorillonite	[1318-93-0]	
magnesium carbonate		[546-93-0]	absorbent
metallic soaps	magnesium stearate	[557-704-0]	hydrophobic, lubricant
	zinc ricinoleate	[13040-19-2]	
silica	fumed	[7631-86-9]	absorbent
	xerogel	[112945-52-5]	
starch	corn starch	[9005-25-6]	hygroscopic
	rice starch	[9005-25-8]	
talc	hydrated magnesium silicate (steatite)	[14807-96-6]	opaque lubricant
titanium dioxide		[13463-67-7]	opaque, white
zinc oxide		[1314-13-2]	opaque, adherent
zirconium silicate		[10101-52-7]	opaque, white

mills to reduce the particle size. Loose powders are filled without additional processing.

If compression is required to provide a stick or pan-type of product, the bulk components must be held together with a binder. Common binders are various lipids, polymers, polysaccharides, and waxes. Some binder compositions include water, which is removed by drying the compact. The amount of binder must be carefully controlled to yield a solid, nonfragile compact that is soft enough to pay off. Excessive amounts of or improperly compounded binders glaze during use because of transfer of skin lipids to the compact.

When the bulk containing the binder is uniform, it is compressed on pneumatic, hydraulic, or ram-type presses. Compression can be carried out in presses provided with suitably designed cavities or in metallic pans. The pans are filled with the powder mass, and a plunger with a cross-sectional shape similar to that of the pan is used to compress the tablet. The resulting tablets are commonly used with powder puffs or cosmetic brushes.

9. Skin Preparation Products

Products for use on the skin are designed to improve skin quality, to maintain (or restore) skin's youthful appearance, and to aid in alleviating the symptoms of minor diseases of the skin. Many of these products are subject to different regulations in different countries. Skin products are generally formulated for a specific consumer purpose.

9.1. Skin-Care Products.

Preparations are generally classified by body part and purpose. For example:

Product	Purpose
baby preparations	
oils and lotions	cleansing, soothing
diaper-rash products	prevention, cure
powders	drying
foot preparations	
antifungals	anti-infective
emollients	soothing, crack-prevention
powders	drying
facial preparations	
lotions and creams	smoothing, protecting, rejuvenating
body preparations	
lotions and creams	smoothing, protecting
oils	smoothing, protecting
powders	drying
hand preparations	
lotions and creams	smoothing, protecting
gels	antichapping

The smoothing or emollient properties of creams and lotions are critical for making these emulsions the preferred vehicles for facial skin moisturizers, skin protectants, and rejuvenating products. On the body, emollients provide smoothness and tend to reduce the sensation of tightness commonly associated with dryness and loss of lipids from the skin. Although a wide variety of plant and animal extracts have been claimed to impart skin benefits, valid scientific evidence for efficacy has been provided only rarely.

Emulsion components enter the stratum corneum and other epidermal layers at different rates. Most of the water evaporates, and a residue of emulsifiers, lipids, and other nonvolatile constituents remains on the skin. Some of these materials and other product ingredients may permeate the skin; others remain on the surface. If the blend of nonvolatiles materially reduces the evaporative loss of water from the skin, known as the transepidermal water loss (TEWL), the film is identified as occlusive. Application of a layer of petrolatum to normal skin can reduce the TEWL, which is normally about 4–8 $g/(m^2 \cdot h)$, by as much as 50 to 75% for several hours. The evaporated water is to a large extent trapped under the occlusive layer hydrating or moisturizing the dead cells of the stratum corneum. The flexibility of isolated stratum corneum is dependent on the presence of water: dry stratum corneum is brittle and difficult to stretch or bend. Thus, any increase in the water content of skin is believed to improve the skin quality.

The ability to moisturize the stratum corneum has also been claimed for the presence of certain hydrophilic polymers, for example, guar hydroxypropyl trimonium chloride [65497-29-2], on the skin. By far the most popular way to moisturize skin is with humectants, some of which are listed in Table 12. It is

Table 12. **Skin Conditioners and Moisturizers**[a]

Material	CAS Registry number	Molecular formula
glycerol	[56-81-5]	$C_3H_8O_3$
2-pyrrolidinone-5-carboxylic acid (PCA)	[98-79-3]	$C_5H_7NO_3$
sodium lactate	[72-17-3]	$C_3H_5NaO_3$
urea	[57-13-6]	CH_4N_2O
cholesterol	[57-88-5]	$C_{27}H_{46}O$
hydrolyzed glycosaminoglycans[b]		
hydrolyzed soy protein	[68607-88-5]	
linoleic acid	[60-33-3]	$C_{18}H_{32}O_2$
tocopheryl acetate	[7695-91-2]	$C_{31}H_{52}O_3$
witch hazel distillate[c]		
sodium hyaluronate[d]		
myristyl betaine	[2601-33-4]	$C_{18}H_{37}NO_2$

[a] Ref. 26 includes a more comprehensive listing.
[b] Mixed polysaccharides from animal connective tissue.
[c] Nonalcoholic steam distillate of parts of *Hamamelis virginiana*.
[d] Sodium salt of hyaluronic acid [9004-61-9].

claimed that humectants attract water from the environment and thereby provide moisture to the skin.

Studies of the interactions between water and the lipid constituents of the stratum corneum suggest that the supply of water per se is not responsible for skin quality and condition. Water vapor from lower layers provides a constant supply of moisture to the epidermis. Instead, the ability of the skin to retain the moisture is critical, and this ability depends on the lipid lamellar bilayers that occupy the spaces between the cells of the stratum corneum (44–46).

In the United States, products claimed to reverse or alleviate the stigmata of facial skin aging are considered drugs. Claims for improvement of fine wrinkling, mottled hyperpigmentation, and roughness associated with photodamage, on the part of products containing all *trans*-retinoic acid [302-79-4], have received some favorable comments from regulatory advisory panels. Other approaches for anti-aging products are based on desquamation by α-hydroxyacids, for example, lactic acid [50-21-5]. Finally, a number of substances, such as hyaluronic acid [9004-61-9] and collagen [9007-34-5], have been claimed to improve the appearance of wrinkled skin (see also ANTIAGING AGENTS).

The amounts and types of lipids used in skin-care products control their application properties. Methods for assessing these characteristics using expert panelists have been described (47).

The ability of skin-care products to supply moisture to the skin remains in question. In the United States, however, the OTC panel has sanctioned the use of skin-protectant ingredients such as glycerin, which may play roles in the skin's water ecology. Products for the care of body skin are similar to preparations formulated for the care of facial skin. Products for overall body care should leave a dry, satinlike finish even though relatively high levels of unctuous lipids are used. Facial night creams may leave the skin somewhat oily, whereas facial day creams must provide a dry finish.

Hand-care products are designed to reduce chapping and cracking, especially prevalent during cold, dry, winter weather. Hand-care products are commonly fortified with various humectants, and products for the elbows and feet may include abrasives. Bath powders impart lubricity to body skin, absorb moisture, and provide some fragrance. These are formulated without pigments to preclude the staining of clothing. Skin-care formulations have been published for skin protectants (48), face creams (49), hand creams (50), and body creams (51).

9.2. Antiacne Preparations. Antiacne products are designed to alleviate the unsightly appearance and underlying cause of juvenile acne. Generally, acne is a mild disease of the follicular duct in which sebaceous secretion is not readily allowed to pass to the surface of the skin because of a hyperkeratotic restriction in the duct. The retained sebum may undergo chemical changes or be altered by microbial species, with consequent inflammatory responses. In the past, cosmetic preparations were designed to remove sebum from the skin surface with solvents or cleansers and work against microorganisms with antibacterials. In addition, acne was cosmetically treated with abrasives in the hope that scrubbing would relieve the ductal blockage.

As of 1991 in the United States, OTC antiacne preparations may contain only a few active drugs, for example, sulfur [7704-34-9], resorcinol acetate [102-29-4], resorcinol [108-46-3], salicylic acid [69-72-7], and some combinations (52). OTC anti-acne constituents may be included in a variety of conventional cosmetic preparations, which then become OTC drugs. These include lotions, creams, solutions, facial makeups, facial cleansers (including abrasive cleansers), and astringents. Products must contain the specified drugs at the designated concentrations. Compositions of antiacne products have been published (53).

9.3. Sunscreens. Radiation that reaches the earth's surface from the sun is limited to wavelengths above about 285 nm because shorter wavelengths are absorbed by ozone (qv). Investigations of the impact of ultraviolet (uv) light on human skin have identified the range from 285 to about 320 nm as uvB and that between 330 nm and visible light as uvA. Both uvA and uvB have the potential to burn skin, resulting in an acute sunburn that is painful and can have damaging long-term effects, such as wrinkling, actinic keratoses, or carcinomas. The flux of uvA and uvB that reaches human skin depends on altitude and latitude. Equatorial regions receive maximum flux. Clouds, dust, and reflected uv light from the ground or water also affect flux and may provide some wavelength specificity to the radiation. The flux required to produce a barely observable erythema, the so-called minimal erythemal dose (MED), depends on the energy of the uv radiation. Thus, much higher fluxes of uvA than of uvB are required for the production of one MED. The estimation of the MED (a rapid skin response) is not a quantitative measure of long-term skin damage, especially because the lower energy uvA penetrates much deeper into the skin than does the shorter wavelength uvB.

The use of uv light absorbing substances is accepted worldwide as a means of protecting skin and body against damage and trauma from uv radiation. These colorless organic substances are raised to higher energy levels upon absorption of uv light, but little is known about mechanisms for the disposal of this energy.

These substances can be classified by the wavelengths at which absorbance is maximal. Absorption throughout the incident uv range (285 to about 400 nm) affords the best protection against erythema.

It is also possible to deflect uv radiation by physically blocking the radiation using an opaque makeup product. A low particle size titanium dioxide can reflect uv light without the undesirable whitening effect on the skin that often results from products containing, for example, zinc oxide or regular grades of titanium dioxide.

In vitro absorption-spectrophotometry techniques are available to assess a sunscreen's efficacy, but the preferred methods are *in vivo* procedures in which a small body site is irradiated with the desired wavelengths for different periods in the presence or absence of a uv protectant. Procedures vary from country to country to determine the incremental timing of the exposure that ultimately allows quantification via sun protective factor (SPF). In the United States, sunscreen preparations are considered OTC drug products, and the SPF must be specified (54). Even in countries that do not identify these products as drugs, SPF labeling has become customary.

The SPF is defined as the ratio of the time required to produce a perceptible erythema on a site protected by a specified dose of the uv protectant product to the time required for minimal erythema development in the unprotected skin. An SPF of 8 indicates that the product allows a subject to expose the protected skin 8 times as long as the unprotected skin to produce the minimum erythemal response. The measurement can be quite subjective unless skin color and the history of reactions to sun exposure of the test subjects are taken into account. The MED range for Caucasians at 300 nm averages 34 mJ/cm^2. The range is 14–80 mJ/cm^2. Perspiration or the use of artificial irradiation devices can create additional problems.

Because perspiration and bathing are commonly associated with sun exposure, the need to determine the SPF after bathing or long after application to the body site is important. In use, the quantity of screen applied and its uniform distribution over the exposed area control the achieved SPF. Methods for assessing the water-resistant or waterproof qualities of sunscreen products have been established by the FDA.

A list of uv absorbing substances found useful in protective sunscreen products is provided in Table 13. Some information on the levels permitted in products in both the United States and the EEC is included. Descriptions and specifications of sunscreens have been published (55).

In principle, emulsified sunscreen products are similar to emollient skin-care products in which some of the emollient lipids are replaced by uv absorbers. The formulation of an effective sunscreen product generally requires combination of a uvB and a uvA absorber if an SPF above about 12 is desired. Two or more of the sunscreens listed in Table 13 normally constitute about one-half of the nonvolatiles found in sunscreen lotions. The other half consists of an emollient (solvent) and emulsifying and bodying agents. If water-resistant qualities are desired, polymeric film formers, for example, acrylates–octylacrylamide copolymers [9002-93-1], or water-repellent lipids, for example, dimethicone [9006-65-9], are included.

Table 13. **Cosmetic Uv Absorbers**

Ingredient	CAS Registry number	Quantity approved, % U.S.[a]	Quantity approved, % EEC[b]
uvA Absorbers			
benzophenone-8	[131-53-3]	3	
menthyl anthranilate	[134-09-6]	3.5–5	
benzophenone-4	[4065-45-6]	5–10	5
benzophenone-3	[113-57-7]	2–6	10
uvB Absorbers			
p-aminobenzoic acid (PABA)	[150-13-0]	5–15	5
pentyl dimethyl PABA	[14779-78-3]	1–5	5
cinoxate	[104-28-9]	1–3	5
DEA *p*-methoxycinnamate		8–10	8
digalloyl trioleate	[17048-39-4]	2–5	4
ethyl dihydroxypropyl PABA	[5882-17-0]	1–5	5
octocrylene	[6187-30-4]	7–10	
octyl methoxycinnamate	[5460-77-3]	2–7.5	10
octyl salicylate	[118-60-5]	3–5	5
glyceryl PABA	[136-44-7]	2–3	5
homosalate	[118-56-9]	4–15	10
lawsone (0.25%)	[83-72-7]		
plus dihydroxyacetone (33%)	[96-26-4]		
octyl dimethyl PABA	[21245-02-3]	1.4–8	8
2-phenylbenzimidazole-5-sulfonic acid	[27503-81-7]	1–4	8
TEA salicylate	[2174-16-7]	5–12	2
sulfomethyl benzylidene bornanone	[90457-82-2]		10
urocanic acid (and esters)	[104-98-3]		2
Physical barriers			
red petrolatum		30–100	
titanium dioxide	[13463-67-7]	2–25	

[a] Ref. 55.

[b] Tentative.

More recently anhydrous sunscreens have become popular. Products of this type are based on blends of emollient lipids and acceptable uv absorbers. Formulations of sunscreen products have been published (56).

9.4. Facial Makeup. This classification applies to all products intended to impart a satinlike tinted finish to facial skin and includes liquid makeups, tinted loose or compressed powders, rouges, and blushers.

In modern liquid makeups and rouges, the required pigments are extended and ground in a blend of suitable cosmetic lipids. This magma is then emulsified, commonly as o/w, in a water base. Soaps, monostearates, conditioning lipids, and viscosity-increasing clays are primary components. Nonionic emulsifiers can replace part or all of the soap. Pigment levels in these emulsions are about 15% but can range as high as 60% if the stabilizing clays are included. The viscosity of these types of preparations varies from fairly thin fluids to thixotropic viscous lotions to firm creams. These products must not dry too rapidly to permit spreading on the skin and feathering of the edges for proper shading.

Tinted dry powders form the second type of facial makeup. Commonly, the blended solids are compressed into compacts. The finished products, sold as compressed powders, rouges, or blushers, are applied to the face with the aid of powder puffs, brushes, or similar devices. Facial makeup compositions have been published for rouge (57), powder (58), and makeup (59).

9.5. Skin Coloring and Bleaching Preparations. Products designed to simulate a tan, to lighten skin color in general, or to decolorize small hyperpigmented areas such as age spots either impart to or remove color from the skin. Skin stains are intended to create the appearance of tanned skin without exposure to the sun. The most widely used ingredient is dihydroxyacetone [96-26-4] (2–5% at pH 4 to 6) which reacts with protein amino groups in the stratum corneum to produce yellowish brown Maillard products. Lawsone [83-72-7] and juglone [481-39-0] are known to stain skin directly. Stimulation of melanin formation is another approach to artificial tanning. Commercialization, which is limited, depends primarily on topical application of products containing tyrosine or a tyrosine recursor.

The number of cosmetically acceptable bleaching ingredients is very small, and products for this purpose are considered drugs in the United States. The most popular ingredient is hydroquinone [123-31-9] at 1–5%; the addition of uv light absorbers and antioxidants reportedly helps to reduce color recurrence. Effective bleaching requires repeated localized applications of a cream or ointment type of preparation. Formulations for skin lighteners (60) and skin darkeners (61) have been published.

10. Astringents

Astringents are designed to dry the skin, denature skin proteins, and tighten or reduce the size of pore openings on the skin surface. These products can have antimicrobial effects and are frequently buffered to lower the pH of skin. They are perfumed, hydro-alcoholic solutions of weak acids, such as tannic acid or potassium alum, and various plant extracts, such as birch leaf extract. The alcohol is not only a suitable solvent but also helps remove excess sebum and soil from the skin. After-shave lotions generally function as astringents.

In the United States, some astringents, depending on product claims, are considered OTC drugs (62). Only three ingredients, aluminum acetate [139-12-8], aluminum sulfate [10043-01-3], and hamamelis [84696-19-5], are considered safe and effective.

10.1. Antiperspirants and Deodorants. There are many forms of antiperspirants and deodorants: liquids, powders, creams, and sticks. Deodorants do not interfere with the delivery of eccrine or apocrine secretions to the skin surface but control odor by reodorization or antibacterial action. Deodorant products, regardless of form, are antimicrobial fragrance products. An important antimicrobial or cosmetic biocide used in many products is triclosan [3380-34-5]. Other active agents include zinc phenolsulfonate [127-82-2], *p*-chloro-*m*-xylenol [88-04-0], and cetrimonium bromide [57-09-0]. There have been claims that ion-exchange polymers and complexing agents provide protection against

Table 14. **Antiperspirant Ingredients**

Name	CAS Registry number	Molecular formula
Aluminum chlorohydrates[a]		
aluminum chlorohydrate	[1327-41-9]; [12042-91-0]	$Al_2(OH)_5Cl \cdot nH_2O$
aluminum sesquichlorohydrate	[11097-68-0]	$Al_2(OH)_{4.5}Cl_{1.5} \cdot nH_2O$
aluminum dichlorohydrate	[1327-41-9]; [12042-91-0]	$Al_2(OH)_4Cl_2 \cdot nH_2O$
Aluminum zirconium chlorohydrates[a,b]		
aluminum zirconium octachlorohydrate		$Al_8Zr(OH)_{20}Cl_8 \cdot nH_2O$
aluminum zirconium pentachlorohydrate		$Al_8Zr(OH)_{23}Cl_5 \cdot nH_2O$
aluminum zirconium tetrachlorohydrate	[57158-29-9]	$Al_4Zr(OH)_{12}Cl_4 \cdot nH_2O$
aluminum zirconium trichlorohydrate		$Al_4Zr(OH)_{13}Cl_3 \cdot nH_2O$
Aluminum salts		
aluminum chloride	[7446-70-0]	$AlCl_3$
buffered aluminum sulfate	[10043-01-3]; [18917-91-4]	$Al_2(SO_4)_3$ and $Al(CH_3CHOHCOO)_3$

[a] Partially dehydrated derivatives complexed with polyethylene glycol or propylene glycol exist. In the United States, derivatives in which some of the water of hydration has been replaced by glycine are particularly popular. Aluminum zirconium tetrachlorhydrex gly and related derivatives can be used in OTC antiperspirant products.

[b] The Al/Zr ratio is variable.

unpleasant body odors. In addition, delayed-release, that is, liposomal or encapsulated, substances of diverse activity have been employed.

The mechanism of antiperspirant action has not been fully established but probably is associated with blockage of ducts leading to the surface by protein denaturation by aluminum salts. The FDA has mandated that an antiperspirant product must reduce perspiration by at least 20% and has provided some guidelines for testing finished products. Some antiperspirant chemicals are listed in Table 14 (63).

Clear solutions of antiperspirants have been on the market for about 100 years. Cream and lotion types are o/w emulsions commonly formulated using nonionic emulsifiers to avoid aluminum salt formation, especially by carboxylic acids. Cream antiperspirants are generally distributed in jars, whereas lotions are dispensed from roll-on types of containers.

Antiperspirant aerosols (qv) can be wet or dry. In the wet type, the antiperspirant chemical is dissolved in a suitable solvent, such as water–ethanol, combined with emollients and so on, and dispensed after pressurization using an acceptable propellant. Dry aerosols may be based on a finely milled antiperspirant component suspended with emollients and suspending agents in a volatile liquid that is lost after dispensing.

Most antiperspirant sticks are molded. Sticks dominate in the U.S. market, whereas lotion and cream antiperspirants are preferred in Europe. Stick antiperspirant products may include suspending agents, coupling agents to wet the antiperspirant chemical (about 20–25%), and emollients. The blend is prepared at about 65°C and poured at about 55°C. Antiperspirant (64) and deodorant (65) compositions have been published.

11. Cleansing Preparations

Cleansing preparations are products, based on surfactants or abrasives, that are designed to remove unwanted soil and debris from skin, hair, and the oral cavity. Soaps (qv) are the best-known cleansers but are not considered cosmetic products unless they are formulated with agents that prevent skin damage or contain antimicrobial agents. Soaps are the least costly and most popular skin cleansers available. Use as hair cleansers is limited, however, by the tendency to form insoluble alkaline earth soaps, which leave a dulling film on hair, and the taste of soaps generally precludes use in oral-care preparations. Soaps dominate the skin cleanser market, although they have been shown in closed patch skin tests to cause some irritation owing to their alkalinity. Modern skin cleansers (liquids and bars) for sensitive skin employ various synthetic detergents (see Table 8).

11.1. Skin Cleansers. Their mildness, foaming qualities, water solubility, and tolerance of slightly acid conditions (pH 5–6) make many of the surfactants listed in Table 8 attractive for use in formulating facial and body cleansers. Irritant qualities of preparations based on one or more of these surfactants can be further modified by the addition of lipids or agents that lower the defatting (drying) tendencies of the finished product.

The solubility characteristics of sodium acyl isethionates allow them to be used in synthetic detergent (syndet) bars. Complex blends of an isethionate and various soaps, free fatty acids, and small amounts of other surfactants reportedly are essentially nonirritant skin cleansers (66). As a rule, the more detersive surfactants, for example alkyl sulfates, α-olefin sulfonates, and alkylaryl sulfonates, are used in limited amounts in skin cleansers. Most skin cleansers are compounded to leave an emollient residue on the skin after rinsing with water. Free fatty acids, alkyl betaines, and some compatible cationic or quaternary compounds have been found to be especially useful. A mildly acidic environment on the skin helps control the growth of resident microbial species. Detergent-based skin cleansers can be formulated with abrasives to remove scaly or hard-to-remove materials from the skin.

Foaming bath and shower preparations are based on blends of surfactants and various conditioning agents, many of which are derived from plants, and may contain a relatively high percentage of fragrance. Surfactants are those identified in Table 8 as being beneficial in facial and body washes. Foam boosters are used to create the billowing foam desired in many of these products; sequestering agents are added to prevent the formation of alkali metal salts, especially when soap is used.

Cream-type skin cleansers have been used for many years, particularly on the face. The classical cold cream consists of mineral oil (50–60%), beeswax ($\simeq$15%), borax ($\simeq$1%), and water (30–40%). Neutralization of the cerotic acid in beeswax by borax yields the emulsifier to form the cream. When applied to the face, the mineral oil acts as a solvent for sebum, soil, and makeup. The remains are tissued off, leaving the skin clean with a lubricating, oily finish. This very simple composition can be modified with additional emulsifiers, thickening agents, and cosmetic additives. There are numerous cosmetic wipe-off cleansers, although the popularity of these oil-based products has declined. When still more emulsifiers, especially water-soluble nonionics, are included, the original wipe-off products are converted into the more popular rinse-off types. The principal cleansing agents in these products are the oily components; in contrast with the detergent-based cleansers, the surfactant is included only to aid in removal of the product during rinsing, not for detergency.

11.2. Hair Cleansers. Except for a few specialty preparations, hair cleansers, or shampoos, are based on aqueous surfactants. The detergents of choice in shampoos are listed in Table 8. The most popular surfactants in shampoos are alkyl sulfates and alkylether sulfates, commonly used at about 10–15% active. These ingredients by themselves do not provide the dense, copious foam desired by consumers, and additives are required, especially for use on oily hair or scalps. The foam boosters usually found in finished shampoos are fatty acid alkanolamides, fatty alcohols, and amine ocides. In the so-called superamide foam boosters the ratio of alkanolamine to fatty acid is 1:1. In addition to about 1–2% of an amide, most commonly the diethanolamide of lauric acid [120-40-1] or of coconut fatty acids [61791-31-9], almost all shampoos contain a hair-conditioning agent. The detergent removes lipids from the hair's surface, leaving hair with limited gloss and often difficult to comb. Hair that has been defatted by detergents has a tendency to retain a static electric charge. The resulting fly-away hair can be avoided by making the hair more conductive by means of moisture or electrolytes or by lubricating the hair with a lipid or conditioning agent. The preferred conditioning agents are materials substantive to hair, that is, not readily rinsed off by water.

Excessive degreasing by shampoos can be overcome by treatment with an after-shampoo (cream) rinse or a hair dressing. It is considered desirable to control the effects of excessive surface degreasing at the time of shampooing. A wide variety of hair-conditioning additives has been recommended and tested. Only a few have gained wide acceptance, for example:

Name	CAS Registry number
dialkyl (C_{12}–C_{18}) dimethylammonium chloride,	eg, [53401-74-9]
hydrolyzed collagen	[9015-54-7]
polymeric quaternary derivatives	eg, [26590-05-6] or [53568-66-4]
potassium cocoyl hydrolyzed collagen	[68920-65-0]
sodium cocoamphoacetate	eg, [68334-21-4]
sodium lauroyl glutamate	[22923-31-7]
stearamidopropyl betaine	[68920-65-0]

Modern shampoos containing one or more of these conditioners have been designated as two-in-one products. They provide good cleaning and leave hair conditioned without the need for a second treatment. Eye stinging and irritation caused by shampoos can be reduced by including nonionic surfactants (with 10–45 polyoxyethylene groups) or by adding an amphocarboxylate.

Dandruff, a benign scaling skin disease of the scalp, is commonly viewed as a hair problem. The etiology and therapy of dandruff are similar to those of seborrheic dermatitis (67). Antidandruff shampoos are formulated using antimicrobial or desquamating agents to reduce the lipophilic yeasts (qv) widely believed to be the cause of scalp flaking. In the United States, shampoos for which antidandruff claims are made are OTC drugs. The choice of active agents is limited to coal tar [8007-45-2], zinc pyrithione [13463-41-7], salicylic acid [69-72-7], selenium sulfide [7488-56-4], and sulfur [7704-34-9], which can be added to shampoos or other scalp preparations. Some of the fungicidal azoles and piroctone olamine (1-hydroxy-4-methyl-6-(2,4,4-tri-methylpentyl)-2-(1*H*) pyridinone, ethanolamine salt [68890-66-4] are active against these causative organisms but are not recognized in United States OTC regulations.

11.3. Oral Cleansing Products. Toothpastes and mouthwashes are considered cosmetic oral cleansers as long as claims about them are restricted to cleaning or deodorization. Because deodorization may depend on reduction of microbiota in the mouth, several antimicrobial agents, either quaternaries, such as benzethonium chloride [121-54-0], or phenolics, such as triclosan [3380-35-5], are permitted. Products that include anticaries or antigingivitis agents or claim to provide such treatment are considered drugs.

Mouthwashes are hydro-alcoholic preparations in which flavorants, essential oils (see OILS, ESSENTIAL), and other agents are combined to provide long-term breath deodorization. Palatability can be improved by including a polyhydric alcohol such as glycerin or sorbitol (see ALCOHOLS, POLYHYDRIC). Occasionally, anionic and nonionic surfactants are used to help solubilize flavorants and to help remove debris and bacteria from the mouth.

Dentifrices (qv), or toothpastes, depend on abrasives to clean and polish teeth. The principal ingredients in toothpastes or powders are 20–50% polishing agents, such as calcium carbonate, di- or tricalcium phosphate, insoluble sodium metaphosphate, silica, and alumina; 0.5–1.0% detergents, for example, soap or anionic surface-active agents; 0.3–10% binders (gums); 20–60% humectants, such as glycerol, propylene glycol, and sorbitol; sweeteners (saccharin, sorbitol); preservatives, such as benzoic acid or *p*-hydroxybenzoates; flavors, for example, essential oils; and water. The most widely used surfactant is sodium lauryl sulfate, which is available with high purity. It produces the desired foam during brushing, acts as a cleansing agent, and has some bactericidal activity.

Transparent dentifrices can be prepared from certain xerogel silicas through use of high levels of polyhydric alcohols. Clarity depends on matching the refractive indexes of the silica and the liquid base. Compositions for liquid facial cleansers (68), shampoos (69), conditioning shampoos (70), dandruff shampoos (71), surfactant bars (72), toothpastes (73), and mouthwashes (74) have been published.

12. Shaving Products

Cosmetic shaving products are preparations for use before, during, or after shaving.

12.1. Preshaves. Preshave products are used primarily for dry (electric) shaving. Solid preshaves are usually compressed-powder sticks based on lubricating solids, such as talc or zinc or glyceryl stearate. Liquid preshaves are intended to remove perspiration residues and tighten and lubricate the skin. The alcohol content is relatively high (50–80%) to accelerate drying. The remaining ingredients may be polymeric lubricants, such as 1–2% polyvinylpyrrolidinone (PVP) [9003-39-8], emollients, such as 1–5% diisopropyl adipate [6938-94-9], and up to about 5% propylene glycol.

12.2. Shaving Creams. Despite the replacement of soap by synthetic detergents, products for wet shaving continue to be based on soap. Shaving creams and soaps are available as solids, that is, bars; creams, generally in tubes; or aerosols. Solids are essentially pure soaps applied to the face as foams with a brush. Shaving creams may be nonlathering (emulsion) and rarely consist entirely of lubricating lipids.

The principal ingredients of shaving creams and aerosols are liquid soaps, usually a blend of potassium, amine, and sodium salts of fatty acids, formulated to create a foam with the desired consistency and rinsing qualities. The soap blend may include synthetic surfactants, skin-conditioning agents, and other components. Modern nonaerosol shaving creams may contain 20–30% soap (potassium or triethanolamine (TEA)), up to about 10% glycerine, emollients, and foam stabilizers. Aerosol shaving creams are dilute forms of the cream types and are dispensed from the container with the aid of hydrocarbon propellants (up to about 10%). Aerosol shaving creams may also include some emulsifiers to ensure uniform emulsification of the propellant during the short shaking period before dispensation.

The objectives of shaving creams include protecting the face from cuts by cushioning the razor. Beard-softening qualities are attributable almost exclusively to hair hydration, which also depends on pH. Lubrication must be provided, primarily between the blade and the hair fibers through which it passes. Blade technology based on polymeric coatings reduces the need for this type of lubrication by shaving creams.

12.3. After-Shaves. After-shave preparations serve the same function as and are formulated similarly to skin astringents. After-shave balms are hydro-alcoholic or alcohol-free emulsions that supply soothing ingredients, for example, witch hazel, and emollients, for example, decyl oleate [3687-46-5], to the skin. Menthol, which provides a cooling sensation, is a common constituent of after-shaves.

Compositions for preshaves (75), shaving creams (76), and after-shaves (77) have been published.

13. Nail-Care Products

Over the years the cosmetic industry has created a wide variety of products for nail care. Some of these, such as cuticle removers and nail hardeners, are functional; others, such as nail lacquers, lacquer removers, and nail elongators, are decorative.

13.1. Functional Nail-Care Products. Cuticle removers are solutions of dilute alkalies that facilitate removal, or at least softening, of the cuticle. Formulations containing as much as 5% potassium hydroxide have been reported. Such preparations may contain about 10% glycerine to reduce drying, and thickeners, such as clays, to reduce runoff. Lipids and other conditioners are included to reduce damage to tissues other than the cuticle.

Nail hardeners have been based on various protein cross-linking agents. Only formaldehyde is widely used commercially. Contact with skin and inhalation must be avoided to preclude sensitization and other adverse reactions. The popularity of products of this type is decreasing because the polymers used in nail elongators can be used to coat nails to increase the mechanical strength.

13.2. Decorative Nail-Care Products. Nail lacquers, or nail polishes, consist of resin, plasticizer, pigments, and solvents. The most commonly used resin is nitrocellulose, prepared by esterification of celluloses with nitric acid, with a degree of substitution between 1.8 and 2.3 nitrate groupings per anhydroglucose unit. Ethylacetate, butylacetate, and toluene are typical solvents. Toluenesulfonamide–formaldehyde resin [25035-71-6] and similar polymers, for example, the terpolymer of 2,2,4-trimethyl-1,3-pentanediol, isophthalic acid, and trimellitic anhydride, are the resins of choice as secondary film formers for optimal nail adhesion. Other resins, such as alkyds, acrylates, and polyamides, can also serve as secondary film formers.

Camphor, dibutyl phthalate [84-74-2], and other lipidic solvents are common plasticizers. Nail lacquers require the presence of a suspending agent because pigments have a tendency to settle. Most tinted lacquers contain a suitable flocculating agent, such as stearalkonium hectorite, a reaction product of hectorite [12173-46-6] and stearalkonium chloride [122-19-0].

The blend of pigments used to create a particular shade must conform to regulations covering pigments and dyes in cosmetics. Regulations vary among countries and undergo frequent changes. The selected pigments may not stain the nails, and any organic dye or pigment that might exhibit solubility in the mixture of lacquer solvents is avoided. Typical organic dyes include monoazo dyes, such as D&C Red No. 6 Barium Lake and D&C Red No. 34 Calcium Lake, and pyrazole dyes, such as FD&C Yellow No. 5 Aluminum Lake (see AZO DYES). Inorganic pigments, such as iron oxides and titanium dioxide, can be incorporated. Colored pigments do not usually exhibit the opacity and reflective brilliance demanded of modern nail enamels. Bismuth oxychloride, mica, and guanine were extensively used in the past to provide nacreous reflections, whereas titanium dioxide provided opacity. These substances have been replaced by the highly reflective and nacreous synthetic mica–titanium dioxide pigments. Generally, nacreous pigments are supplied as suspensions in nitrocellulose-containing solvent blends, whereas other pigments are mixed with nitrocellulose and plasticizers and processed through a roller mill. Nitrocellulose processing must be done with extreme caution in an explosion-proof environment. The level of pigment in nail enamels generally does not exceed about 5%. The solvent level is about 60–70%, however, and the dried lacquer may contain as much as 10–15% pigment.

Nail lacquer removers are simply acetone or blends of solvents similar to those used in nail lacquers. It is commonly accepted that solvents have a drying effect on nails, and nail lacquer removers are often fortified with various lipids such as castor oil [8991-79-4] or cetyl palmitate [540-10-3].

Nail elongators are products intended to lengthen nails. These have become extremely popular. In earlier compositions, polymerization was conducted by mixing monomers, oligomers, and catalysts on the nail (78). More recently, nail elongation is achieved by adhering a piece of non-woven nylon fabric (referred to as nail wrap) to the nail with a colorless lacquer. This process may be repeated until the desired nail thickness has been reached. After shaping, the artificial nail is further decorated. Compositions for nail lacquers (79) and nail hardeners and conditioners (80) have been published.

14. Hair Products

Cosmetics for hair care fall into several categories: cleansers or shampoos, conditioners, fixatives, coloring products, waving and straightening products, and hair removers (see HAIR PREPARATIONS).

14.1. Hair Conditioners. Hair conditioners are designed to repair chemical and environmental damage, replace natural lipids removed by shampooing, and facilitate managing and styling hair. The classical hair-conditioning products were based on lipids, which were deposited on hair either directly, with oils or pomades, or from emulsions. Liquid and semisolid brilliantines are formulated from mineral oil or vegetable or animal fats thickened with waxes (ozokerite), fatty alcohols (cetyl alcohol), or polymers (for example, polyethylene), and are normally dispensed from jars or tubes. Emulsion products are commonly based on an oil phase that consists of mineral oil, lanolin, and synthetic or vegetable-derived lipids. The emulsifiers vary widely and may include anionics (soap), nonionics (alkyl polyoxyethylene ethers), or cationics (eg, PEG-2 stearmonium chloride [606087-87-8]). These o/w type emulsions may be thickened with various gums and may contain plant extracts, antimicrobial agents (quaternaries), uv screens, and hair-fixative polymers such as PVP.

Microemulsions, temporary emulsions, that is, two-layer hair dressings, and clear solutions of nonvolatile lubricants are on the market. Hair tonics, usually hydro-alcoholic, achieve similar effects by including lipid substances or synthetic emollients, such as the mono butyl ethers of polypropylene oxides [9003-13-8] (10–50 mol). The primary benefits of these lipid-based products are lubrication and improvements in hair gloss and hair-holding (dressing) qualities. Hair holding and manageability result from the tendency of the lipid components to make the fibers adhere to each other laterally, not from the coating of individual hairs.

An entirely different, and in the 1990s more popular, type of hair conditioning is achieved by treating hair with substantive quaternary compounds or quaternary polymers. Quaternaries are sorbed by hair, retained despite rinsing with water, and removed only by shampooing. Quaternaries that are not easily removed cannot be used, because they tend to build up on the hair, making it overconditioned and limp. The most widely used quaternary is stearalkonium chloride [122-19-0], which has been used at 3–5% concentration in cream rinses for many years. More recently, many useful quaternaries have become available; some are listed in Table 15. Table 15 also includes some quaternary polymers that are not only substantive to hair but also possess hair-fixative properties. Despite the commercial success of many conditioning quaternaries, efforts to synthesize better performing derivatives continue.

Table 15. **Hair-Conditioning and Polymeric Fixative Compounds**[a]

Material	CAS Registry number
Hair conditioners	
disoyadimonium chloride	[61788-92-9]
hydroxyethyl cetyldimonium chloride	[24625-03-4]
stearalkonium chloride	[122-19-0]
quaternium 22	[51812-80-7]
quaternium 79 hydrolyzed milk protein[b]	
Hair conditioners with fixative properties	
polyquaternium 4[c]	
polyquaternium 6	[26062-79-3]
polyquaternium 7	[26590-05-6]
polyquaternium 10	[53568-66-4]
polyquaternium 11[d]	
polyquaternium 22	[53694-17-0]
Hair-fixative polymers	
polyvinylpyrrolidinone (PVP)	[9003-39-8]
shellac	[9000-59-3]
vinyl acetate–crotonic acid–vinyl neodecanoate copolymer	[55353-21-4]

[a] Ref. 26 includes a more comprehensive listing.

[b] Material is the reaction product of a fatty acid amide of *N,N*-dimethylpropylenediamine and epichlorohydrin and hydrolyzed milk protein.

[c] Dialkyldimethyl ammonium chloride–hydroxyethylcellulose copolymer.

[d] Vinylpyrrolidinone–dimethylaminoethyl methacrylate copolymer, dimethyl sulfate reaction product.

A third type of hair-conditioning product relies on the use of proteins, amino acids (qv), botanicals, and amphoterics. Many ingredients have been identified as hair conditioners. Some of them are claimed to be substantive to the hair, whereas others are claimed to penetrate into the hair and repair previously incurred damage. Some of these hair-conditioning substances have been incorporated into newer delivery systems, such as mousses. These water-based products are dispensed as foams, which are rubbed into the hair and may then be rinsed off with water or allowed to remain on the hair for conditioning and styling benefits. All types of hydrolyzed proteins, such askeratin, soy, yeast, and wheat, chemically modified and free amino acids, such as cystine, aspartic acid, and lauroyl glutamate, and biological additives, such as casein, beer, eggs, nettle extract, and horse chestnut extract, have been formulated into products containing amphoteric and other more conventional cosmetic ingredients. Reference 26 includes an extensive list of chemicals used in hair conditioners and related products.

14.2. Hair Fixatives. These products are designed to assist in hair styling and in maintaining the style for a period of time. In contrast with hair dressings, hair fixatives do not leave an oily residue on the hair but tend to coat the hair with film-forming residues after drying. As in the case of hair dressings, style-holding qualities depend primarily on fiber–fiber adhesion and to a minor extent on fiber coating. The products may be conveniently divided into two groups: those that are applied to damp or wet hair, hair-setting products, and those that are applied to hair after styling, hair sprays. Styling requires that hair be formed into and retain the desired configuration. Curlers of various designs provide a wavy style, whereas hot combing results in essentially straight hair.

Wave-setting products can be applied to wet hair and should not interfere with or delay drying. Such products commonly aid in wet styling of hair. After drying, these products are claimed to help retain the style, regardless of frequent combing or exposure to high humidity. Wave sets can be formulated with water-soluble polymeric substances or with polymers that show solubility only in hydro-alcoholic media. Some of the preferred hair-fixative polymers (see Table 15) are combined with lubricants or emollients and other excipients. The viscosity of these products can vary from that of a water-thin fluid to a rather firm gel. The set-holding polymer constitutes about 1–3% of the product, and the viscosity-increasing substance is commonly a cross-linked polyacrylate, for example, carbomer [9007-16-3].

Hair sprays are applied from aerosol cans or pumps to dried and styled hair. Hair-spray products containing little or no water are preferred, because the presence of significant levels of water tends to soften a preexisting style. In the past, hair sprays were alcoholic solutions of polymers that were propelled with fluorinated or chlorinated highly volatile solvents. The alcohol concentration was kept as low as possible to reduce excessive wetting. As a result, the fixative resins had to exhibit good solubility in the propellant blends. Environmental regulations today preclude the use of these propellant solvents. Thus higher levels of alcohols are now used and the propellants of choice are low concentrations of hydrocarbons.

14.3. Hair Colorants. Hair colorants are commonly divided into temporary, semipermanent, and permanent types. Decolorizing (bleaching) represents a fourth type of hair coloring (81) (see BLEACHING AGENTS).

Hair bleaching removes the pigment melanin from the hair shaft by oxidative destruction. Alkaline hydrogen peroxide is the agent of choice. Because hydrogen peroxide is unstable at elevated pH, it is frequently supplied in pure form (6–10%) and is combined at the time of use with an ammonia or an amine-containing product to provide approximately 3–6% H_2O_2 at a pH of about 8.5 to 9.5. Thickening is required in order to retain the blended oxidizing mixture on the hair. Thickeners and conditioning agents, for example, fatty alcohols and protein derivatives, can be formulated into the alkalizing component or, occasionally, into the hydrogen peroxide. Surfactants are required to assure that every hair fiber is thoroughly wet by the blended mixture. Bleaching by hydrogen peroxide is enhanced by the presence of a peroxydisulfate, such as potassium persulfate [7727-21-1]. Bleaching damages the hair by converting some cystine to cysteic acid. In addition, the high pH induces swelling and cuticular damage. These adverse effects are counteracted by conditioning after treatment or by including some protectants in the hair-bleach product.

Temporary hair colorants are removed from the hair by a single shampoo. Temporary hair colorants usually employ certified dyes that have little affinity for hair (see Table 9). They are incorporated into aqueous solutions, shampoos, or hair-setting products.

Semipermanent hair colorants employ dyes that are absorbed directly by the hair. These dyes add color to the preexisting (natural) hair color and are

Table 16. **Semipermanent Hair Dyes**[a]

Name	CAS Registry number	CI Number	Chemical type
Pigment Violet 19	[1047-16-1]	46500	quinacridone
Pigment Yellow 13	[5102-83-0]	21100	diazo
Basic Violet 3	[548-62-9]	42555	triarylmethane
Basic Red 76	[68391-30-0]	12245	monoazo
Direct Red 80	[2610-10-8]	35780	tetraazo
Disperse Blue 1	[2475-45-8]	64500	anthraquinone
HC Blue 2	[33229-34-4]		nitro-*p*-phenylenediamine
HC Yellow 4	[52551-67-4]		nitroaniline

[a] Ref. 26 includes a comprehensive listing.

useful primarily for blending in gray fibers. These dyes may fade significantly owing to exposure to sunlight and also are gradually removed by shampooing. Dyes selected for this purpose should not stain the scalp or skin during application. Typically, temporary hair colorings are distributed as pourable lotions. Formulations may include alkanolamides, polymeric substances, fatty alcohols, thickeners, and conditioners commonly employed in all hair cosmetics. The chemical nature of the dyes is highly diverse and varies among manufacturers. Solvents, carriers, or complex solubilizers may be required when pigments are used. The CTFA lists temporary hair dyes with other substances as “Color Additives—Hair Colorants” (26). A few key chemical types are identified in Table 16.

Development of the desired shade depends to a large degree on the tendency of the individual dyes in the mixture to adhere to the hair in proper proportions. Performance evaluation on many different types of hair, for example, natural, bleached, and permanently waved, is required.

Permanent hair colorants, frequently identified as oxidation dyes, show much greater resistance to fading and shampoo loss than do semipermanent hair colorants. As a rule, these dyes remain on the hair; it is common practice to dye only that portion of the hair shaft that has emerged from the scalp since the last application. In permanent dyeing, a lotion containing developers and couplers is blended with hydrogen peroxide and then applied to the hair. The objective is uniform penetration of the various components into the hair, oxidation of the developer to a reactive intermediate, and formation of a colored dye stuff with the coupler. The dyes are synthesized within the fiber and migrate outward only slowly because of their size. In addition, the reactions occur in alkaline media, and some of the peroxide bleaches the hair. Thus it is possible to generate colored hair lighter than the original shade. Dye formation is complex because shading is achieved by employing several developers and several couplers in the same dye bath. The process is illustrated by *p*-phenylenediamine, which is oxidized by the peroxide to a quinone diimine. This short-lived intermediate can react, for example, with resorcinol to yield a brownish indoaniline. Table 17 provides some insight into the many interactions that exist from just a few components. Further shading is possible by including semipermanent colorants (see Table 16), especially nitroaniline derivatives.

In hair coloring a light ash blond shade may require as little as 0.5–1% of intermediates, whereas a true black may require up to about 5%. In principle,

Table 17. **Intermediates Used in Oxidation Hair Dyes**[a]

Material	CAS Registry number	Molecular formula
Developers		
4-amino-3-nitrophenol	[119-34-6]	$C_6H_6N_2O_3$
p-aminophenol	[123-30-8]	C_6H_7NO
2-methoxy-*p*-phenylenediamine sulfate	[42909-29-5]	$C_7H_{10}N_2O \cdot xH_2SO_4$
p-methylaminophenol	[150-75-4]	C_7H_9NO
p-phenylenediamine	[106-50-3]	$C_6H_8N_2$
N-phenyl-*p*-phenylenediamine	[101-54-2]	$C_{12}H_{12}N_2$
phloroglucinol	[106-73-6]	$C_9H_6O_3$
toluene-2,5-diamine	[95-70-5]	$C_7H_{10}N_2$
Couplers		
o-aminophenol	[95-55-6]	C_6H_7NO
2,4-diaminophenoxyethanol HCl	[66422-95-5]	$C_8H_{12}N_2O_2 \cdot 2HCl$
2,6-diaminopyridine	[141-86-6]	$C_5H_7N_3$
hydroquinone	[123-31-9]	$C_6H_6O_2$
1,6-naphthalenediol	[83-56-7]	$C_{10}H_8O_2$
m-phenylenediamine	[106-45-2]	$C_6H_8N_2$
pyrocatechol	[120-80-9]	$C_6H_6O_2$
pyrogallol	[87-66-1]	$C_6H_6O_3$
resorcinol	[108-46-3]	$C_6H_6O_2$

[a] Ref. 26 includes a comprehensive listing.

the formulator blends precursors that yield red, blue, and yellow dyes. The base in which the components are dissolved or suspended is similar to that used in simple bleaches and may include alkanolamides, various types of surfactants, thickening agents, and solvents. Removal of undesirable dyes is achieved by treating the discolored hair with a powerful reductant of the sulfite family.

Permanent coloration can also be achieved by exposing hair to certain metals: copper, silver, and especially lead salts. Preparations containing aqueous solutions of lead acetate may include a source of sulfur, usually thiosulfate, which may react with cystine in the hair to produce some cysteine or may react directly with the metal ion to form dark metallic sulfides. Preparations of this type, which darken hair gradually, are not universally considered safe.

14.4. Hair Waving and Straightening Products. The development of hair-waving and hair-straightening products requires a careful balance between product performance and hair damage. The hair-waving process essentially depends on converting some cystine cross-links in keratin to cysteine residues, which are reoxidized after the configuration of the hair has been changed. Sometimes hair straightening can also be achieved by a similar, relatively innocuous chemical change in the hair. As a rule, however, much more chemical destruction is required to achieve rapid and permanent straightening than to achieve permanent waving.

Permanent waving depends on the metathesis of a mercaptan and the cystine in hair while the hair is held in a curly pattern on a suitable device (curler). The most commonly used mercaptan is thioglycolic acid [68-11-1], although some other nonvolatile mercaptans can be employed. The active species is the mercaptide anion. Thus, adjustment to a pH between about 8.8 and 9.5 using amines or especially ammonia is required. A typical hair-waving product may consist of a 0.5–0.75 *N* solution of thioglycolic acid adjusted to a pH of about 9.1 with ammonia. The product generally includes a nonionic surfactant, to ensure thorough wetting of the wound hair tress, and a fragrance. Opaque lotion products can be created by adding the actives to mineral oil or other lipid-containing emulsions. The thioglycolate lotion is allowed to remain on the hair for about 10–30 min; then the hair is rinsed with water. Next, an oxidizing solution consisting of a dilute (1.5–3%) acidified hydrogen peroxide solution or of a potassium or sodium bromate is applied to the hair. This so-called neutralizing solution oxidizes the cysteine residues to cystine (without bleaching) in a new configuration within about 5–10 min. The neutralizer may contain a variety of hair conditioners and is removed from the hair by thorough rinsing with water after unwinding.

Alternatively, the metathesis can be effected by sulfites or bisulfites that convert cystine into one cysteine residue and one thiosulfate (Bunte salt) residue. Hair waving based on sulfites is slower than that based on mercaptans and is more likely to cause changes in hair color.

Acidic waving systems based on mercaptans have recently achieved some popularity. The preferred mercaptan is glyceryl thioglycolate [30618-84-9], which is relatively odorless and provides sufficient active anionic mercaptide species at a neutral pH.

Hair straightening is more difficult than hair waving. Kinky hair has a tight crimp that cannot be straightened by winding over a rod or curler. Two processes for straightening exist. One, based on thioglycolates, effects the same chemical change as that occurring during permanent waving. The other, more aggressive, process is based on (1–8%) sodium hydroxide (or guanidine). The exact concentration depends on the temperature at which the process is carried out. In order to hold the hair straight, hair-straightening products are viscous. The hair is combed repeatedly during the process, which has the effect of reconfiguring the hair but can lead to serious hair damage from excessive pulling. The chemical reactions with sodium hydroxide involve formation of cysteine and dehydroalanine residues in the hair with some loss of sulfur. The cysteine and dehydroalanine can subsequently react to form the thioether, lanthionine [922-55-4], which helps repair the mechanical strength of the fiber to some extent. Similar chemical reactions occur when steam is allowed to interact with hair, such as during hot pressing, which was an earlier technique for straightening hair.

Conditioners, lipids, acid rinses, and related cosmetics have been developed to minimize hair damage from these rather destructive processes.

14.5. Hair Removers. Hair removers are designed to remove hair from the skin surface without cutting in order to avoid undesirable stubble. Cosmetic products have been developed for chemical destruction of hair, that is, depilation, and for facilitating mechanical hair removal, that is, epilation.

Depilatories epitomize the chemical destruction of hair and allow hair removal by scraping with a blunt instrument or by rubbing with terry cloth. Chemical depilatories are based on 5–6% calcium thioglycolate in a cream base (to avoid runoff) at a pH of about 12. The pH is maintained with calcium or strontium hydroxide. Hair destruction is rapid, requiring not more than about 10 min.

Treatment with a depilatory is followed by careful rinsing with water and various conditioning products intended to restore the skin's pH to normal. This type of treatment does not destroy the dermal papilla, and the hair grows back.

Epilation is required for permanent hair removal. The most effective epilation process is electrolysis or a similar procedure. Epilation can also be achieved by pulling the fibers out of the skin. For this purpose, wax mixtures (rosin and beeswax) are blended with lipids, for example, oleyl oleate, which melt at a suitable temperature (about 50–55°C). The mixture is applied to the site (a cloth tape may be melted into the mass) and after cooling is rapidly pulled off the skin. A similar process can be carried out with a tape impregnated with an aggressive adhesive.

Compositions have been published for cream rinses (82), hair conditioners, dressings, and mousses (83), hair-styling products (84), hair sprays (85), hair colorants (86), hair-waving products (87), hair-straightening products (88), and depilatories (89).

15. Decorative Cosmetics

Decorative cosmetics are products intended to enhance appearance by adding color or by hiding or deemphasizing physical defects. In Western cultures, most decorative cosmetics are for use on the face. Products in this category are various types of powders, facial makeups, and lip- and eye-coloring products. Regardless of the site of application or the type of product, all decorative cosmetics must meet certain critical performance criteria as outlined in Table 18. The dyes and pigments used in these products must be stable in the finished

Table 18. **Performance Criteria for Decorative Cosmetics**

Characteristic	Typical components	Comment
covering power	titanium dioxide	hides defects
	zinc oxide	
	magnesium oxide	
	zirconium silicate	
slip	talc	easy application
	zinc or magnesium stearate	smooth sensation
	starch	
	emollient lipids	
absorbency	chalk	absorbs skin secretions
	silica	without color change
	starch	
	synthetic polymers	
adherence	emollient lipids	clings to skin
	volatile solvents	limits ruboff
	polymeric substances	dries to hard film
	gums	
pigmentation	certified pigments	provides color
	noncertified pigments	

preparation and must not fade or discolor as a result of exposure to the variable environment of the skin.

15.1. Lip Makeups. Intensely pigmented coloring products have been used for many years to accentuate and modify the appearance of the lips. These products are marketed in soft stick forms (lipstick), as pastes (tinted lip gloss), and as hard sticks (lip liner). Lipsticks are manufactured via the molding process. The brilliant colors required for lipsticks are produced primarily by a limited number of available organic dyes and lakes. Formulation of acceptable shades is difficult and subject to the vagaries of fashion. For many years, lipsticks that caused a permanent stain on the lips were popular. Such staining is no longer desirable, and skin-staining dyes such as eosin (D&C Red No. 21) are rarely used. Traces of an inoffensive fragrance and of an antioxidant are commonly included in the lipid base (see Table 10). Sophisticated lipsticks may also contain moisturizers and uv light screens.

High gloss lipsticks use castor oil or 2-octyldodecanol. The more wear-resistant fat-based sticks are generally somewhat duller. There is a large number of possible ingredients, but the performance of most sticks is comparable. Feathering of the lipstick film, that is, creeping of color into crevices surrounding the lip tissue, is avoided by controlling the rheological properties of the applied stick mass.

Tinted and untinted soft lipstick masses are distributed in pans as lip glosses. These are applied with the fingers or with lipstick brushes. Hard, tinted, pencil-type sticks have been marketed as lip liners. Chap sticks are unpigmented lipsticks intended to alleviate scaling and to prevent cracked lips. Compositions of lipsticks, lip glosses, and chap sticks have been published (90).

15.2. Eye Makeup. Since antiquity, eye makeup preparations have been used to beautify the area surrounding the eye. Various forms of eye shadows color the eyelid; mascaras color and lengthen the eyelashes; eyeliners delineate the portion of the eyelid from which the eyelashes emerge. The appearance of eyebrows can be altered with various types of makeup, and, finally, false eyelashes and eyebrows have been marketed for years.

In the United States the use of coal-tar dyes in eye makeup is generally prohibited. The use of permanent and temporary hair colorants (Tables 16 and 17) and of organic dyes and their lakes is precluded. As a result, only insoluble inorganic pigments can be used (Table 9). The sensitivity of the eye mandates that coarse or irritating particulate matter not be used. All eye preparations must be properly preserved and, preferably, self-sterilizing to prevent accidental introduction of pathogens into the eye.

Eye shadows may be molded or compressed. The technology used for molded sticks resembles that used in lipsticks except that the choice of pigments is restricted. Glossy lipids are generally avoided. If gloss is desired, it is achieved by the inclusion of a nacreous pigment. The basic technology for producing compressed eye-shadow sticks or powder compacts is that of other powder products.

Mascaras are available in three basic forms: cakes; creams; and mascaramatics, narrow containers provided with brushes. Cakes are commonly prepared by milling pigments into (sodium) soap chips and compressing this blend into metal or plastic pans. A small brush wet with water is used to transfer the mascara to the eyelashes. Cake mascaras can be modified with ingredients that improve adhesion of the mascara to the eyelashes, for example beeswax [8006-40-4] and dihydroabietyl alcohol [26216-77-31]; resist washing off or smearing by tearing, for example, aluminum mono-, di-, or tri-stearates; and lengthen the hairs (polymeric fibrous filaments).

Cream mascaras are pigmented, viscous, o/w emulsions; soap emulsions are common. Viscosity is increased with glyceryl monostearate to help suspend the pigment. Cream mascaras are distributed in small jars or narrow-orifice tubes and are applied with brushes.

Mascaramatic mascaras have the largest share of the market. Emulsion mascaramatics are cream-type mascaras dispensed from containers that include a closure provided with a wand ending in a small brush. In solvent mascaramatics, mascara masses are pigment suspensions in thickened hydrocarbon solvents such as isoparaffins and petroleum distillates. The thickeners include waxes (microcrystalline [63231-60-7], carnauba [8015-86-9], or ouricury [68917-70-4], polymers (hydrogenated polyisobutene [61693-08-1]), and esters (propylene glycol distearate [6182-11-2] or trilaurin [538-24-9]).

Mascara pigmentation is usually black or brown–black. Mascaras during and after application are extremely close to the cornea, and any potential irritant must be rigidly excluded. The use of lash-elongating synthetics, such as rayon, nylon, and the like, has not resulted in significant problems.

The use of false eyelashes is rare. These are prepared from natural or synthetic fibers attached to a tinted lash strip, which can be glued onto the lid with the aid of an adhesive.

Eyeliners are available in two popular forms. One of these is a deeply pigmented emulsion that is applied with a fine brush. The emulsion must be viscous to avoid running and should dry to a waterproof film. The emulsion can be patterned after the emulsions used in mascaras. Glossy eyeliners require the use of nacreous pigments suspended in polymeric film formers, for example, acrylic acid copolymers.

The second type of eyeliner is a soft crayon, in pencil form, that delivers mass with minimal pressure. Products of this type may contain as much as 70% talc, 5% pigment, and 5% aluminum stearate. The lipid portion may include squalene [111-02-4]and alkanolamides.

Eyebrow pencils are used to outline the brow, especially after plucking of undesirable fibers. They are commonly prepared by stick molding. Eyebrow pencils are generally harder than eyeliner pencils. Like other pencils, the extruded mass is normally encased in wood. Some eyebrow pencils may be quite soft, approaching the texture of lipsticks.

Formulations of eye shadows (91), mascaras (92), and eyeliners (93) have been published.

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Martin M. Rieger
M & A Rieger, Associates