

SURFACE-ACTIVE AGENTS IN COSMETICS*

By HARRY C. SPEEL

Antara Products, New York, N. Y.

THE TASK OF CHOOSING the proper surface-active agent to use in formulating specific cosmetic products is often a complex problem. Evidence of this is found in the numerous lists and attempts to classify the hundreds of such agents that are offered to formulators in virtually every field of industrial activity (2, 4, 17, 23, 28). Actually, the total consumption of surface-active agents by cosmetic manufacturers is relatively small, probably less than 5 per cent of the available production. But the existence of thousands of cosmetic manufacturers with their millions of customers makes the cosmetic field a potential customer for almost every new product the chemical manufacturer can make. If the new agent is not quite suitable, he will try to "tailor-make" one more suitable, thus further increasing the available number.

The term "surface-active agent" is, of course, a broad one applied to organic chemicals used for wetting, penetrating, emulsifying, dispersing, solubilizing, foaming, and detergency. Personally, I like the definition of a surface-active agent being a product which brings unlike

surfaces together closer, faster. It imparts a sort of "sex appeal," a quality widely advertized for certain soaps. Indeed, soap is the oldest and best known of all surface-active agents made by man. These agents are all characterized by their ability to modify the surface properties of the medium to which they are added. For example, most agents will make water wetter, though certain types are superior as penetrating wetters and others excel as spreaders. One kind of agent will cause a liquid to foam; another will kill foam. Emulsifying types help make oil and water mix and stay mixed. Dispersion of solids in a liquid is aided by certain agents; other agents reverse the process. No one product excels in all applications. The problem is to classify these agents and to match their peculiar properties with the needs of formulation of specific products.

The primary functions of a surface-active agent are the result of proper blending, or balancing, of the raw materials from which it is made. Synthetic surface-active agents, like common soap and agents that occur in nature, are the result of a combination in one molecule of a water-seeking or hydrophilic portion, and an oil-seeking lipophilic, or hydro-

* Presented at the December 3, 1947, Meeting, New York City.

phobic portion. Molecules of this type orient themselves at the surface of a liquid, and also at the interface between two immiscible liquids. The water-seeking hydrophilic part stays in the water surface, while the oil-seeking hydrocarbon portion of the molecule stays out above the surface, as it were, or finds a non-aqueous medium, thus bringing unlike surfaces together closer, faster. The hydrophilic portion may be either ionic or non-ionic, as exemplified by carboxylate, sulfate, sulfonate, quaternary ammonium, polyhydroxylic and polyoxyethylene residues. The hydrophobic part consists of hydrocarbon chain or ring systems as are found in natural fats (26) and petroleum products (29). So many varied combinations are possible that products can be "tailor-made" to give whatever blend or balance of properties may be desired (1, 9, 27, 30).

CLASSIFICATION

The alphabetical listing of products by brand name or trade name permits a start on more complicated methods of classification. Such lists (17, 25, 28) are continually being revised, as are alphabetical listings of manufacturers and their specialties (25). The next logical step is the alphabetical listing of those agents used, or advocated for use, in specific fields. Beeler's report to the American Pharmaceutical Association (2) and the bulletins prepared by Cupples of the U. S. Dept. of Agriculture's Bureau of Entomology and Plant Quarantine (4) are examples of this. Another method of classifying is by chemical structure. Separation of anionic, cationic, and non-ionic

types can be made in such a grouping (23) as is given in Table 1, where

R = long chain paraffinic or olefinic group—usually C_8 to C_{22}

R' = primary or secondary, straight or branch-chain lower alkyl group—usually C_4 to C_{10}

A = anion—Cl, Br, I, HSO_4

Ar = aryl group—phenyl, naphthyl, diphenyl, etc.

M = alkali metal, ammonium or substituted ammonium, e.g., Na, K, triethanolamine.

This example of chemical classification is obviously only a starting point. It is certainly possible to subdivide cationics and non-ionics also on the basis of whether the hydrophilic group is in the center or at the end. Phosphonates and borates could go up in the anionic grouping instead of being put in miscellaneous. The sulfonium compounds could be added to the cationic group. The fatty amide condensates offer an unusual example of products difficult to classify; they are compatible with soap and some anionic agents, as well as with a number of cationics; they seem to be mildly anionic on the alkaline side and mildly cationic under acid conditions; their chemical structure is a matter of debate. It is also possible to manufacture surface-active agents which contain cationic groupings as well as anionic groupings, e.g., the betaines (alkyl glycines). Nevertheless, the grouping of surface-active agents by differences in chemical structure is of value.

TABLE 1—CHEMICAL CLASSIFICATION OF SURFACE-ACTIVE AGENTS

Group	Formula of Typical Representative	Type	Type Description
A	Anionic—Terminal Hydrophile Group		
	RCOOM	1	Soap
	ROSO ₂ OM	2	Fatty Alcohol Sulfate
	RCONHC ₂ H ₄ OSO ₂ OM	3	Sulfated Hydroxyethyl Amide
	RCOOC ₂ H ₄ OSO ₂ OM	4	Sulfated Fatty Acid Partial Ester
	RCH ₂ OOCCH ₂ SO ₂ OM	5	Fatty Alcohol Sulfoacetate
B	RArO(C ₂ H ₄ O) _n C ₂ H ₄ OSO ₂ OM	6	Sulfated Polyglycol Ethers
	Anionic—Central Hydrophile Group		
	(R') ₂ CHOSO ₂ OM	1	Sulfated Secondary Alcohol
	R'CHR'	2	Sulfonated Hydrocarbon
	SO ₂ OM		
	R ₂ ArSO ₂ OM	3	Alkyl Aryl Sulfonate
C	R'OOCCH ₂ CHCOOR'	4	Sulfonated Ester of Alcohols and Dibasic Acids
	SO ₂ OM		
	Cationic—Usually Terminal Hydrophile Group		
	[RN(CH ₃) ₃] ⁺ A ⁻	1	Long-Chain Quaternary Ammonium Salt
	[R-Pyridine] ⁺ A ⁻	2	Alkyl Tertiary Aryl Ammonium Salt
	[RNH ₃] ⁺ A ⁻	3	Long-Chain Amine Salts
D	Non-ionic		
	RCOOC ₂ H ₅ (OH) ₂	1	Polyhydric Alcohol Partial Fatty Acid Ester
	RCOOC ₂ H ₅ O(OH) ₃	2	Anhydro Polyhydric Alcohol Partial Ester
	RCH ₂ O(C ₂ H ₄ O) _n C ₂ H ₄ OH	3	Fatty Alcohol Polyoxyethylene Ether
	RCOOC ₂ H ₅ O[O(C ₂ H ₄ O) _n C ₂ H ₄ OH] ₃	4	Polyoxyalkylated Anhydro Polyhydric Alcohol Fatty Acid Ester
	RArO(C ₂ H ₄ O) _n C ₂ H ₄ OH	5	Alkyl Phenol Polyoxyethylene Ether
E	Miscellaneous		Hydrophobe-hydrophile Phosphates, Phosphonates, Borates, Fatty Amides, etc.

A few generalities based on general experience are hard to avoid. For example, compounds derived from the lauryl hydrophobic radical are usually superior as wetting and penetrating agents. The myristyl, cetyl, and stearyl hydrophobes constitute the best potential radicals for detergency and emulsification. Most commercially important, synthetic wetting agents and detergents are to be found in groups A and B of

Table 1. But where heavy metal salts or complex cations are apt to be encountered, the tendency of anionics to form insoluble salts often makes them unsuitable, or less suitable than the non-ionics of group D, for detergency or other operations. The agents of group C are attracted by negatively charged substances but repelled by positively charged substances, and are apt to be more stable than anionics in the presence

of concentrated acids, alkalis, and saline solutions. So cationics find use in marine paints and varnishes, in carbonizing wool, in certain textile softeners. Their germicidal applications are well known. The agents of group D tend to act as spreaders, or surface wetters, and are widely employed as emulsifiers. Unfortunately for any hope of successful classification along these lines, no one group has a very strong monopoly on any particular set of properties.

In actual practice physical and chemical combinations of two or more of these agents are often used. Thus compatibility becomes an important factor—one readily found on testing but one not evident in usual methods of classification. One example is the use of glyceryl monostearate, a non-ionic, in emulsion creams using soap formed *in situ* as the major emulsifier. Combinations of two different fatty amides, or two non-ionics are also well known to everyone. The textile field, with its softening oils, and the war-time program of oiling woolen blankets, has shown the value of utilizing anionic or cationic agents combined with non-ionics to give stable emulsions that are substantive to fabrics, animal hair, and inanimate objects; carrying over of these techniques to cosmetic items is on the increase.

COSMETIC PROPERTIES

What properties, other than those shared in common by all surface-

active agents, are important to cosmetic applications? Physical form, appearance, color, odor, sometimes even taste, and cost per pound certainly deserve consideration. Differences in physical properties, such as foaming ability, or physical form, or chemical stability under conditions of usage are naturally very important factors. Most of these properties are obvious as soon as a sample of the product and technical data are made available to the cosmetic chemist. The requirements of specific formulations therefore enable him to pick out a score or more possibilities out of hundreds of agents available.

Dermatological aspects are of primary importance (20). The product should be safe when applied to the skin under possible condition of usage. Incidentally this means that even toxicity on ingestion must be considered (3, 21, 22), for children and their pets may try to eat or drink the product. There is also evidence that wetting agents may bring about penetration of the skin, if not directly perhaps through emulsification and transfer to the glands (11).

A recent study by Dodd, Hartmann and Ward (6) on surface-active agents as potential irritants in ointment bases is worthy of note. Nine surface-active agents were tested for irritant properties on rabbits and human beings. In the series only the ionic surface-active agents were irritating to human skin, while the non-ionics were non-irritating. Their data seems to

preclude alkalinity, *per se*, as the cause of irritation from surface-active agents. Blank (18) has stated that neither the alkali nor the fatty acid alone is the cause of soap dermatitis; he believes each is a factor. According to Mumford, the organic sulfonates and sulfuric acid esters appear to remove natural fat from the skin and may therefore act as irritants. Duemling's work (7) indicates surface-active agents may possess the ability to penetrate the skin, perhaps indirectly, which Lane and Blank (14) suggest as a possible cause of cutaneous irritation. These and many other dermatological studies indicate the possibility of ionic character being related to skin irritant action.

Patch tests (8) on the surface-active agent alone, or on aqueous dispersions of the agent, serve only as a guide to safety. In most cosmetic products the surface-active agent is only a minor ingredient. In shampoos the synthetic detergent may be the major ingredient. Shampoos, however, are seldom used daily and are thoroughly rinsed away after use. So the conditions of usage as well as the concentration must be considered. Furthermore, there is evidence in the literature (15) that skin irritation levels of a given agent depend on more factors than time and concentration; for example, a 3 per cent aqueous solution may be non-irritating though 3 per cent in a fatty cream or ointment may cause irritation.

EVALUATION

Assuming it is safe to consider usage in a cosmetic product, what other tests are apt to be helpful in the choice of proper surface-active agent? Consideration of a few publicized methods may be of help.

The well-known Draves Test, developed for the textile industry, indicates how rapidly an aqueous dispersion of a synthetic will wet textile fabric under standard conditions. The good penetrating wetters can be compared by the test, but not the surface wetters. Some of the non-ionics lower the surface tension of the water to a greater degree than may anionic or cationic agents, but the non-ionics generally have poor Draves Test results. Personally I believe there may be some connection between Draves Test effects and penetrating ability on human skin, but it is difficult to prove.

Surface tension and interfacial tension lowering effects may be measured, and are generally reported in the manufacturer's literature. Ability to lower interfacial tension is undoubtedly tied up with emulsifying ability. The Spreading Coefficient, which is mathematically derived from surface and interfacial tension measurements (4), seems to be a means of distinguishing to some degree between penetrating and surface wetting agents. It ought to have value to the cosmetic chemist, perhaps even more than the Draves Test.

The development of "water num-

ber" as a method of evaluating absorption bases and emulsifiers has been discussed by deNavarre (5). A recent paper presented by W. C. Griffin detailed some refinements in techniques of measurement.

The solubility characteristics of the agent, while an inherent property, afford a means of choice between various agents for such jobs as emulsifying, solubilizing, etc. War-time government studies on emulsifiers for kerosene and other solvents showed that an agent would not give stable emulsions unless it was reasonably soluble in the solvent. No fully sulfonated product was soluble in, or would emulsify, kerosene; only the non-ionics were satisfactory emulsifiers, and only certain of them.

APPLICATIONS

Detailed discussion of applications and properties of surface-active agents is too lengthy for the purpose of this article, but certain properties and needs can serve as guideposts, deNavarre (5) has divided cosmetic products into creams, lotions, powders, make-up, soap, and miscellaneous. Similarly surface-active agents can be grouped by their primary functions as wetting agents, detergents, emulsifiers, solubilizers, dispersing agents, and miscellaneous.

For creams and lotions, which are mainly mixtures of oils and water, emulsifiers are of primary importance. Most surface-active agents have some emulsifying ability, but in general a product is primarily a

wetting agent or primarily a detergent, or excels in some one specific field. The best emulsifiers for cosmetic oil-and-water systems are generally not the top notch detergents or penetrants and *vice versa*.

Lack of solubility in the oil phase, even in the presence of water, seems to eliminate most of the commercial alkyl aryl sulfonate types, and virtually all commercial products containing salts, as primary cosmetic emulsifiers. Most anionic and cationic agents are not acceptable as sole emulsifiers for one or more reasons, including solubility characteristics, possible skin irritation factors, inability to give easily prepared emulsions of long stability, color, odor, etc. The non-ionics are free from most of these objections, so the problem is to pick the one that most nearly fits the requirements of a specific formulation.

An emulsifier that is primarily oil-soluble tends to produce water-in-oil emulsions. A water-soluble surface-active agent will produce oil-in-water type emulsions. This rule of Bancroft seems to hold pretty well for simple emulsions with one emulsifier. Sometimes, of course, it seems that technique of preparation is even more important (13). And synergistic effects, or the use of stabilizing emulsifiers that may or may not have similar solubility characteristics, are often used to increase or decrease emulsion stability. The use of thickening agents, such as certain stearate esters or natural gums, which may or

may not be surface active, is often a technique for improving emulsion stability by mechanical means.

The use of two or more surface-active agents in one formula, to accomplish the synergistic effects just mentioned, can perhaps be considered a trend. While experience has proved synergistic effects must occur in certain empirically devised formulas, it seems that only recently has there been any recognition of the possibility of a scientific basis for such combinations. Prediction is still difficult; the combination may possess the desired properties of both agents, or the undesired ones, or the good may cancel out the bad. Obviously anionic and cationic agents should not be used together, but there are many examples of combinations of agents that are compatible. Thus in formulating a liquid bubble bath, it has been found advantageous to use an alkyl aryl sulfonate or a fatty alcohol sulfate with fatty amides. The use of a small amount of W/O emulsifier in an O/W formula often exerts a stabilizing effect; the reverse is also true, as most emulsions of good stability seem to contain small amounts of both phases. Data on interfacial tension measurements of combinations gave us a lead on that. Combinations of synthetics with soap are increasing in number, despite the almost inevitable loss of some foam-producing value. The solubilizing effect of one synthetic on another is often used to give clarity or to promote stability or ease of dispersion.

The ability of certain surface-active agents to dissolve essential oils, such as water-insoluble perfume oils, and to carry the dissolved oil into an apparently clear solution in water, is an interesting property. Among these products are certain of the fatty amides and some of the polyoxyalkylated fatty acids and their esters. Use in colognes, after-shave lotions, theater sprays, and pine oil bath oils is well known.

For cosmetic products requiring foaming properties, the fatty alcohol sulfates (24), the alkyl aryl sulfonates (10), some of the fatty amides and the amine soaps compete with normal soaps (12, 16). But where non-foaming detergency is required, as in cleansing creams and lotions, mineral oil combined with a non-ionic ester or non-foaming fatty amide emulsifier is indicated. Since the time of contact with the skin is short, the limitations of skin irritation effects is less important in shampoos, bubble baths, hair wave lotions, and the like. It is obviously more important in shaving creams and products that are used under conditions involving stringent mechanical action, even though they may be removed within a few minutes. In products involving hours of contact, all ingredients are contributory (19). The net result is that the number of surface-active agents that can be considered for utilization increases as we go from emulsion cream formulation to detergent and foaming types of cosmetic items.

Solid, water-free cosmetic products such as lipstick, rouge, and face

powder seldom utilize surface-active agents. The important exceptions include powdered detergents and bubble bath items. Yet surface-active agents occasionally have some properties, such as solubilizing action on dyes and dispersing action for pigments, or antifoam action, that indicate potential value in the production stages. It is generally a case of balancing desirable against unwanted properties.

No one product can have all the properties desired by all chemists, even for a specified end usage. That is, incidentally, one reason why there is the trend toward synergistic combinations. It is evident that the cosmetic chemist must not only work with surface-active agents but also must choose those most likely to work for him. Dermatologic aspects, as evidenced by patch tests on raw material as well as finished product, are one of his most important guides. Classifications of surface-active agents by chemical structure and by major fields of usage (e.g., emulsifier, detergent, etc.) further serve as a means of selecting logical agents with which to work.

And last, but not least, articles in the scientific literature as well as the suggestions on formulation furnished by suppliers of cosmetic raw materials can often be of real help on specific problems.

BIBLIOGRAPHY

- (1) Adam, N. K., "The Physics and Chemistry of Surfaces," Clarendon Press, Oxford, 3rd Edition (1941).
- (2) Beeler, E. C., "Hydrophilic Ointments and Bases," *Bull. Natl. Formulary Comm.*, **10**, Nos. 8 and 9 (1943).
- (3) Benaglia, A. E., Robinson, E. J., Utley, E., and Cleverdon, M. A., "The Chronic Toxicity of Aerosol OT," *J. Ind. Hyg. Tox.*, **25**, 175 (1941).
- (4) Cupples, H. L., "List of Commercially Available Wetting, Dispersing and Emulsifying Agents," U. S. Dept. Agr., Bur. Ent. & Plant Quarantine, Bull. E-504 (June, 1940).
- (5) deNavarre, M. G., "The Chemistry and Manufacture of Cosmetics," D. Van Nostrand Co., New York (1941).
- (6) Dodd, M. C., Hartmann, F. W., and Ward, W. C., "Surface Active Agents as Ointment Bases," *J. Am. Ph. A., Sci. Ed.*, **35**, 33 (1946).
- (7) Duemling, W. W., "Wetting Agents. New Synthetic Chemicals of Use in Finer and More Efficient Dermatological Therapy," *Arch. Dermatol. Syphilol.*, **43**, 264 (1941).
- (8) Durfee, G. R., "Skin Irritation Studies on Selected Subjects," *Proc. Sci. Sec. Toilet Goods Assn.*, No. 7 (May 16, 1947).
- (9) Goldsmith, H. A., "Polyhydric Alcohol Esters of Fatty Acids. Their Preparation, Properties and Uses," *Chem. Rev.*, **33**, 257 (1943).
- (10) Harris, J. C., "Shampoo Formulation," *Am. Perfumer & Essent. Oil Rev.*, **48**, 54 (Nov.); 71 (Dec.) (1946).
- (11) Hermann, F., Sulzberger, M. B., and Baer, R. L., "New Penetrating Vehicles and Solvents," *Science*, **96**, 451 (1942).
- (12) Hilfer, H., "Soapless Detergents," *Drug & Cosmetic Ind.*, **58**, 646 (1946).
- (13) Hollenberg, I. R., "Emulsion Technology," *Ibid.*, **59**, 340 (Sept.); 644 (Nov.) (1946).
- (14) Lane, C. G., and Blank, I. H., *J. Am. Med. Assoc.*, **118**, 804 (1942).
- (15) Macias-Sarria, J., "Sodium Lauryl Sulfate as an Emulsifier," *Am. Perfumer & Essent. Oil Rev.*, **48**, 61 (1946).
- (16) McCutcheon, J. W., "Detergents. Synthetic vs. Soap," *Soap & San. Chem.*, **37**, 37-42 (Sept., 1946).
- (17) McCutcheon, J. W., "Synthetic Detergents. Main Types, Uses, Properties and Prospects," *Chem. Indus.*, **61**, 811-24, (Nov., 1947).
- (18) "Medicinal Uses of Soap," edited by Dr. Morris Fishbein, J. P. Lippincott Co., Philadelphia (1946).
- (19) Schwartz, L., "Protective Ointments and Industrial Cleansers," *Medical Clinics of North America*, **1195** (July 1942).
- (20) Schwartz, L., and Peck, S. M., "Cos-

- metics and Dermatitis," Paul B. Hoeber, New York (1946).
- (21) Smyth, H. F., Jr., Seaton, J., and Fischer, L., "Some Pharmacological Properties of the 'Tergitol' Penetrants," *J. Ind. Hyg.*, **23**, 478 (1941).
- (22) Smyth, H. F., Jr., Seaton, J., and Fischer, L., "The Single Dose Toxicity of Some Glycols and Derivatives," *J. Ind. Hyg. & Toxicol.*, **23**, 259 (1941).
- (23) Speel, H. C., "Surface-Active Agents, Chemical Types and Applications," *J. Invest. Derm.*, **6**, 293 (1945).
- (24) Stassel, E., "Fatty Alcohols," *Soap & San. Chem.*, **38** (Aug., 1945).
- (25) "Textile Chemical Specialty Guide," Textile Book Publishers, New York. Issued annually.
- (26) "The Chemistry of Fatty Acids," Armour & Co., Chem. Div., Chicago (1947).
- (27) Tomlinson, K., "The Design of Surface Active Molecules," *Mfg. Chem. & Mfg. Perf.*, **15**, 249 (1944).
- (28) Van Antwerpen, F. J., "Surface Active Agents Manufactured in America and Commercially Available," *Ind. Eng. Chem.*, **35**, 126 (1943).
- (29) Wakeman, R. L., and Weil, B. H., "ABC of Chemical Derivatives from Petroleum," *Natl. Petroleum News*, R-161 (April 7, 1943).
- (30) Young, C. B. F., and Koons, K. N., "Surface Active Agents," Chemical Publishing Co., Brooklyn (1945).
-