

COSMETIC FUNCTIONS OF SYNTHETIC DETERGENTS*

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QUITE REGULARLY in the history of chemical technology there have become available radically new materials which stimulate and facilitate rapid advancement in widely divergent fields. The introduction of such materials is usually followed by a period of intensive development during which specialists investigate them and attempt to utilize their novel characteristics to fullest advantage. For some time, we have been in such a stage with regard to the synthetic surface-active agents. Cosmetic technologists have not lagged behind the leaders in taking advantage of these new substances. The basic purpose of this paper is to indicate some of the interesting specific characteristics of surface-active agents, and to consider how they might be utilized to an even fuller potential. The more general physical and chemical properties of the surface-active agents have been amply surveyed and are by now quite familiar. A brief review of the more important points will, however, serve to orient the subsequent discussion.

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With respect to chemical structure the surface-active agents are characterized by having a highly unsymmetrical molecule, one portion of which is *polar* and *hydrophilic*, with high residual valency. The other portion of the molecule is *non-polar* and *hydrophobic*. Depending on the relative influence of these two portions the material will be primarily oil-soluble or water-soluble, although many common surface-active agents are soluble in both types of solvent. The oil-soluble substances are of considerable technical importance but this discussion will be concerned largely with the water-soluble series. These products may be classified primarily according to the nature of the hydrophilic group as shown in Table 1.

A second basis for classification is the nature of the hydrophobic group. In commercial detergents this group is seldom, if ever, molecularly uniform. It usually consists of a mixture of isomers or homologues belonging to the same series. The more common series of hydrophobic groups are: (1) The straight chain aliphatic hydrocarbon groups of 8 to 18 carbon atoms, derived di-

TABLE 1—CLASSIFICATION OF SURFACE-ACTIVE AGENTS ACCORDING TO HYDROPHILIC GROUPS

I. Ionogenic
A. Anionic
1. —COOH
2. —O—SO ₃ H
3. —SO ₃ H
4. Phosphoric and miscellaneous
B. Cationic
1. Non-quaternary nitrogen bases
2. Quaternary nitrogen bases
3. Non-nitrogenous
C. Ampholytic
II. Non-Ionic
A. Polyhydroxy compounds
B. Polyether compounds

rectly or indirectly from the natural fatty acids. (2) Branched chain aliphatic hydrocarbon groups derived from kerosene or polymerized lower alkenes. (3) Branched chain aliphatic hydrocarbon groups derived from purely synthetic sources, e.g., 2-ethylhexanol. (4) Alkyl aromatic hydrocarbon groups, in which the alkyl group is usually branched, and ranges from 3 to 20 carbon atoms. (5) Terpene groups, derived from rosin and similar sources.

A third basis for classification is the nature of the group which serves to link together the hydrophobic and hydrophilic portions of the molecule. The main types of linkage are: (1) Direct linkage as in the fatty alkyl sulfates or alkyl aromatic sulfonates, (2) ester groups, (3) acid amide groups, (4) ether groups. It is apparent, even from this highly abridged classification system, that several hundred different *types* of surface-active compounds and almost innumerable individual products may be prepared. There are commercially available today about

30 different types represented by some hundreds of individual products. Relatively few are available in pure form but most manufacturers will furnish data on the nature and extent of the diluents or other substances in the mixture. All of these types and individual products differ quantitatively from one another in their surface active properties, and a very wide choice of surface behavior or characteristics is accordingly available to the technologist.

From the physical chemist's point of view the surface-active agents are soluble substances whose primary characteristic is their power to lower the surface tension of their solutions to an extraordinary extent. This effect is intimately related to a strong adsorption of solute molecules or ions at the phase boundaries of the solution. An equally important characteristic of surface-active agents is the strong association of their molecules or ions in solution. The associated particles or micelles are large enough to confer the typical properties of a colloid to the solution. The association reaction is reversible and rapidly assumes an equilibrium state. Surface-active solutions are accordingly molecularly dispersed in extremely dilute solutions and only assume the typical associated micellar form when a certain critical concentration range is reached. This critical region for most common surface-active agents is in the neighborhood of 0.01 to 0.5 per cent.

The technologist regards surface-

active agents as substances whose dilute solutions may promote wetting, spreading, penetration, emulsification, detergency, foaming or similar important utilitarian effects. It should be emphasized that these effects are neither clearly distinct from one another nor mutually exclusive. They are complex phenomena, difficult to define quantitatively, whose molecular mechanisms have been explained only in a qualitative manner. The distinction between detergents, wetting agents, emulsifying agents, etc., is a deceptive oversimplification in terminology. It stems from some of the pioneering application work on surface-active agents in the textile industry, and has lost much of its significance as the number of individual applications in other industries has multiplied. It has become accepted usage to employ the less cumbersome word "detergents" for the whole range of surface-active agents as well as for those products which exhibit outstanding cleaning power in a given system. The distinction in meaning is usually quite apparent, from the context.

The practical utility of any detergent may be limited or promoted by a number of properties not related to surface activity. Among these are solubility, chemical reactivity, physical form, color, and odor. Of the two detergents which were well known before the present era, soap is limited by its instability toward hydrogen ions and heavy metal ions; the sulfated oils are limited by their physical form and lack of

chemical homogeneity. With literally hundreds of new detergents now available it is usually possible to find a product with just the right combination of physical, chemical, and surface-active properties to fulfill any desired function, including many functions which heretofore could not be fulfilled at all.

The cosmetic industry has been quick to take advantage of this situation. Among outstanding examples are the newer cream formulations and the latest shampoos. Creams based on acid-resistant anionic detergents and non-ionic detergents are much more versatile than the older soap-based creams. Many of the modern depilatory creams, antiperspirant creams, and medicated creams could not possibly be formulated on a soap base. The synthetic detergent shampoos, which function well regardless of water condition, have surpassed the traditional liquid soaps in popularity. Numerous specialized items such as bubble baths, certain liquid cream lotions, and skin cleansers for soap-sensitive individuals depend on synthetic detergents of one type or another. Many modern industrial skin and hand cleansers depend on synthetic detergents rather than on soaps, and the success of synthetic detergents in dentifrices is well established. These spectacular successes have been achieved largely by cut and try methods, with little emphasis on the theoretical basis underlying the utilization of detergents. The field of emulsions and emulsification is a possible

exception to this rule. The theory of emulsions has been extensively studied and discussed in the literature, and is part of the working equipment of the cosmetic chemist. The fundamental factors involved in wetting, penetration, foaming, and detergency, however, are less well recognized, and it is logical to suppose that their application would facilitate even greater efficiency and effectiveness in the use of synthetic detergents. This point might best be illustrated by considering a few specific examples, the first of which concerns skin cleansing preparations.

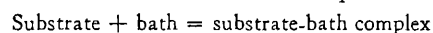
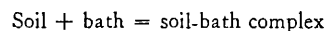
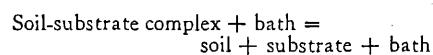
Cleansing of the skin is essentially a problem in detergency, and much of the knowledge gained in studying detergency on fabrics, metals, ceramics, etc., is directly applicable to this problem. A detergative system consists of three essential elements:

1. A solid object to be cleaned, called the substrate. In this case it is the human skin.

2. Water-insoluble "soil" or "dirt" attached to the substrate. The soil may consist of several phases but a typical soil is a mixture of liquid oily material with finely divided solid material.

3. A "bath" which consists essentially of a dilute aqueous solution of the detergent. The total bath rather than the relatively small amount of detergent dissolved in it must be considered as the cleaning agent. The dissolved detergent confers enhanced cleaning properties to the bath, but the bath may contain builders, protective

colloids, and other effective ingredients in addition to the primary detergent. The cleaning operation itself may be represented by the equations:



The course of these reactions is determined only by those observable factors which determine the course of any similar chemical reaction, namely:

1. Nature of the soil.
2. Nature of the substrate.
3. Composition of the bath.
4. Relative quantities of soil, substrate, and bath.
5. Physical conditions of operation, including temperature, duration, and mechanical agitation.

The molecular mechanisms involved in disrupting the soil-substrate complex vary with the individual system concerned. Among those which are known to occur, separately or concurrently, in various systems are:

1. Differential wetting of the substrate by the bath and the soil, i.e., a decreasing of the contact angle at the substrate-soil-bath boundary line. This effect is connected with adsorption of surface-active ions or molecules on soil and substrate.
2. Electrostatic or coulombic effects, conditioned by the adsorption of ions of high specific charge.
3. Protective colloid effects, conditioned by the adsorption of

- surface-active micelles or other colloids in the bath.
4. Solubilization of the soil.
 5. Emulsification of liquid soils.
 6. Deflocculation and suspension of solid soils.

Detailed consideration of these mechanisms is, however, of far less practical importance than the directly observable factors listed above.

The skin, considered as the substrate in a detergative system, is unusually complex. Neglecting the pores (for the time being) the outermost surface of the skin consists of a reasonably smooth layer of flat, dead keratinized cells. Except in specialized areas this layer, the stratum corneum, is so thin that the sensory nerves in the living layers below can easily perceive minor disturbances on the surface. The dead superficial cells are continuously being removed by external attrition and by the progressive maturing and outward migration of new cells from the lower layers. In the last stages of their attachment to the body it might be difficult to decide whether they are part of the substrate or part of the soil. With regard to their permeability, soil-binding power and reactions toward the bath they are probably quite similar to a hair or a wool fiber. This relatively simple picture is complicated, however, by the presence of the several million skin glands and their open pores. The lining of these pores consists of living unkeratinized epithelial cells and certainly has markedly different

properties from the stratum corneum. The sudoriparous glands secrete a clear fluid and thus tend to keep themselves clean and free of foreign soil. The sebaceous glands secrete the products of their own necrosis including solid, oily, and aqueous cell debris. The solid debris tends to clog the pore of the gland and in this light it can be regarded as undesirable soil. When successfully excreted, however, the sebum spreads over the stratum corneum and forms an oily protective layer, which is said to "lubricate" the skin. This lubrication is desirable since it renders the surface less liable to abrasive injury. The sebum probably has no direct effect in making the epidermal layers more pliable, after the manner of oil in tanned leather. It doubtless has an indirect effect, however, since the thin oily layer inhibits the evaporation of moisture and consequent desiccation of the skin.

It is apparent that a precise definition of desirable cleanliness with regard to the skin is highly elusive, and is essentially a problem for the dermatologist. Certainly all solid and most liquid soil of foreign origin should be removed. It might also be desirable to remove excesses of oily or solid sebum from the stratum corneum. It is questionable whether the sebum should be removed completely, although it would probably be desirable to remove excess solid cell debris from the canals of overactive sebaceous glands before they become clogged and give rise to an acne condition.

In this connection the problem arises as to whether a detergent solution is capable of cleaning out the skin pores and, if so, to what depth and how rapidly. It is a widespread and understandable fallacy to suppose that those detergents which show the highest wetting power by a Draves test or a Seyferth-Morgan test must necessarily penetrate the skin pores most effectively. This is not the case. The canals of the skin glands form a typical capillary system. Washburn's equation for the rate of penetration of a liquid into a capillary is:

$$\frac{dl}{dt} = \frac{(rG \cos \theta)}{4lV}$$

where r is the radius of the capillary, G is the surface tension, θ is the contact angle, l is the distance in the capillary, and V is the viscosity. When θ is zero the rate of penetration is proportional to the surface tension/viscosity ratio. When θ is between zero and 90° , high surface tension actually promotes penetration. This implies that detergents will aid the penetration of a capillary mass only where the contact angle at the capillary walls must be reduced to below 90° . Practically any detergent will reduce the contact angle to below 90° , and the best penetration should therefore be attained by agents of relatively high surface tension and low viscosity. This effect has actually been checked in the case of textile fabrics. It is noteworthy that wetting and spreading, as measured by the spreading coefficient, S , depends on

a zero contact angle and very low values of surface and interfacial tensions.

$$S = G_b - G_a - G_{ab}$$

where the G s are the surface tensions of the substrate b , the spreading liquid a , and the interfacial tension between a and b . A liquid which would be ideal for wetting and spreading over the stratum corneum would accordingly be slow to penetrate the pores, and *vice versa*.

Another consideration of great importance in skin cleansing is the adsorption of the detergent itself on the skin. This problem is intimately connected with the subjective sensation or "feel" associated with the detergent, and the objective symptoms of irritation such as might be observed by a dermatologist. It is well known that certain synthetic detergents cause complaints of dryness. The writer is unaware of any quantitative measure of the dryness of skin, but the explanation is often advanced that these particular synthetic detergents "defat" the skin. This explanation is at best incomplete. All detergents including soap, under normal conditions of use, will remove sebum thoroughly. So will rubbing alcohol, which tends to make the skin feel moist, and look shiny rather than dry. Certainly none of the detergents can remove fatty matter from the interior of the cells in either the stratum corneum or the lower strata of the skin. A more comprehensive hypothesis of the drying action of detergents takes

into account the deposition of an adsorbed layer of the detergent on the skin. It has been proved that most detergents leave an adsorbed layer of their own molecules on textile fibers after having removed all the original soil. Soap is known to leave a layer of fatty acids and acid soaps on textile fibers and also on the skin.

These layers may have a variety of effects. If no layer is left and the pore linings are not injured as in the case of rubbing alcohol, the sebum soon builds up and the skin feels normal. A layer of free fatty acid deposited from neutral soap, or of glyceride oil deposited from sulfated oils, feels normal and pleasant to most individuals and apparently does not disturb normal functioning of the skin. The adsorbed layer of a "drying" detergent may possibly exert a tanning action on the keratinized outer cells, or it may adversely influence the living cells in the pore linings, thus diminishing the flow of sebum. The adsorbed layer may also, by its chemical nature, evoke the sensation of "dryness" in the nerve endings without objectively disturbing the skin functions. These are speculations, and have as yet no positive claim to validity. They are not, however, contradicted by any known facts concerning the interaction of detergent and substrate in a deterative system. They are supported by the fact that the various detergents differ markedly in their drying effect on skin and this drying effect bears no relationship to their efficiency as oily

soil removers, at least as measured on fabrics. The writer is unaware of any quantitative tests on the power of various detergents to remove sebum from skin. Some very poor detergents such as the lower alkyl naphthalene sulfonates feel extremely drying on the skin, whereas some excellent detergents such as the alkyl aryl ether sulfates leave the skin feeling bland and pleasant. The above considerations hold true at comparable pH values, and although pH is known to have a marked effect on cutaneous reactions it is not the decisive factor in this case.

With regard to shampoos the above picture is somewhat further complicated. The scalp and hair normally carry a higher soil load than the skin and the mechanical difficulties of cleansing are therefore magnified. The semidetached, keratinous, dead cells tend to accumulate on the scalp in the form of dandruff, and these must be removed. Any adsorbed film left on the hair must be lustrous and non-tacky and should contribute to rather than detract from the softness and manageability of the hair. Drying effect on the scalp is fully as important as it is in the case of skin cleansers. The possibility and effect of adsorbed films on both hair and scalp must accordingly be considered. It should be noted that a detergent which leaves a lustrous, clean, soft hair shaft might nevertheless leave a tight dry feeling on the scalp and thus be unsatisfactory to the user.

These examples indicate that the study of detergent effects in cosmetic preparations could be put on a more fundamental basis and that the current theories of detergency, although admittedly incomplete, could serve as a useful guide in such studies. A somewhat more complicated example is found in the emulsion creams. In using most creams the object is to spread a thin layer of the oily component on the skin and to use the aqueous component merely as a carrier. The problem of producing a satisfactory stable emulsion of good spreading properties has been thoroughly studied. The behavior of such an emulsion on contact with the skin, however, is less well known. In many cases it is not known whether the emulsions break or remain stable on contact with skin and hair, although it is well known that contact with a foreign solid phase often causes emulsions to break. It has proved possible, in the case of metals and fabrics at least, to formulate emulsions which will break as desired, with either the oil phase or the water phase clinging to the substrate. This could quite possibly be done in the case of cosmetic creams. The nature of the detergent or emulsifying agent is the major controlling factor in this phenomenon. Among the numerous products now available it is probable that combinations can be found which will cause the emulsion to break in either manner or not to break at all.

In shaving cream one of the essential problems is the removal and

dispersion of the oily constituents which are added to increase the smoothness, lubricity, and emollient effect on the face. In this case a detergent of very high oil-dispersing power must be sought. This property must, of course, be coupled with the other well-known essential properties, but oil-dispersing power is relatively easy to measure and varies enormously among the different detergents. The synergy of various surface-active combinations with regard to emulsifying or oil-dispersing power has been emphasized in several recent publications, and some of these findings can doubtless be applied directly to the development of more rinsable shaving creams.

Dentifrices present a problem which seems well suited to a straightforward study of detergency. Here the nature of the substrate, tooth enamel, is well known and can even be simulated reasonably well by artificial mixtures. The nature of the soil, the so-called "dental plaque" is less well recognized, but could probably be ascertained with no more than normal difficulty. The detergent must act in a diluted saliva medium, and it is known that the soil-substrate bond in this case is very strong. There is no doubt that a wide variation in tooth cleaning power exists among the different individual detergents as well as among the different types. It is also possible that a systematic study of dental detergency would point the way toward an optimum tailor-made detergent, superior to

the present products which were developed for general use rather than for specific use in dentifrices. Such a program would require close co-operation among a group of specialists, and would doubtless be costly, but the chances for improvement over even the more recent formulas would be significant.

In conclusion the following points may be summarized and emphasized:

1. The synthetic chemistry of detergents has advanced to a point where numerous different types and their various generic properties are well recognized. Not only are hundreds of individual products known, but the possibility exists for synthesizing or formulating innumerable others with reasonably good chances of predicting their properties.
2. The physico-chemical principles underlying detergency, wetting, emulsification, and other phases of surface activity are sufficiently well understood so that individual problems can be soundly analyzed and need not be attacked solely by laborious empirical methods.
3. The organic and physical branches of the science of detergency are already being successfully combined and applied in textile processing, metal cleaning, laundering, and other branches of technology.
4. Although the limitations imposed by the sensitive and living nature of the human skin are severe, it is highly probable that a similar intensive application of the newly developed science of detergents to cosmetology would result in corresponding advances. In fact, these very limitations make the scientific approach, and the utilization of the fundamental knowledge now available, much more attractive than the purely empirical approach.