

SHAMPOO FORMULATION*

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CONSIDERING THE wide variety of surface-active agents commercially available, it is interesting to note that the cosmetic industry utilizes so relatively few of these materials in shampoo formulation. These favored products are almost, without exception, fatty acid soaps or fatty derivatives of the anionic type; they enjoy a sort of historical priority and this accounts, at least in part, for their preferred position. However, there does not seem to be any reason why many of the neglected materials may not find some useful place in shampoo manufacture if properly formulated or purified. One barrier to the more efficient utilization of available materials has been the development of some rather interesting misconceptions regarding surface-active agents and the effects which they produce.

A blanket objection often raised against synthetics is that they are excessively drying or defatting. The literature, however, is sadly lacking in evidence that the synthetics differ significantly from soap as to efficiency in removing fatty materials

from protein fibers. Evidence of actual extraction from the skin of lipoids by aqueous solutions of detergents is also unavailable. There appears to be a division of opinion among dermatologists on such matters as permeability of the skin to water or its ability to absorb fat dispersed in surface-active solutions. While there is no reason to doubt that surface-active agents do remove surface oils from the hair and skin, it is well to bear in mind that these surface oils are excretions and, secondly, that the sebaceous glands are continuously replacing these surface oils. It might also be pointed out that at least some lipoid material on epithelial surfaces is in a "bound" state and is not readily removed under any but the most stringent conditions. Stoves (1) reported that the medulla of kolinsky fur fiber contained a lipoid-protein which will not yield its fatty component (sterol) on extraction with chloroform or with synthetic detergent but is hydrolyzed only by boiling with 7.5 per cent alcoholic sodium hydroxide for two hours.

In view of the absence of conclusive data on the removal of subsur-

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face lipoids, it may be desirable to describe the so-called defatting reaction of synthetics in sensory terms. If the hands are washed with a relatively concentrated solution of purified neutral C₁₂ alkyl aryl sulfonate, a copious lather with good lubricating properties may be worked up. As the hands are rinsed and as the suds disappear, one becomes aware of the abrupt development of a high coefficient of friction making it very difficult to pass one palm over the other; a peculiar crackle is also produced. On towelling the hands a tackiness may be noted but this disappears on complete drying. If the hands are rewetted, the high coefficient of friction of the skin is again evident. This sensation is generally believed typical of ultra-clean skin. Now if this is true defatting there are several facts which are rather difficult to explain: (1) Short chain alkyl naphthalene sulfonates which are notoriously poor detergents and fat emulsifiers produce the same effects as the high molecular weight alkyl aryl sulfonates while oleic acid soaps, which are generally conceded to be excellent fat emulsifiers, do not "dry" the skin. (2) Real defatting of the skin with organic solvents does not produce effects similar to those obtained even with the most powerful neutral synthetic detergents. (3) The skin of the palms, where the "drying" effect of the synthetics is most pronounced, is notably lacking in sebaceous- or oil-secreting glands. These circumstances suggest that actual defatting of the

skin may not be a satisfactory explanation for the phenomenon just described.

The effects produced on the skin by synthetics may be better described as "scoop" to borrow a term from the textile industry—this is a finish imparted to silk by treating with dilute organic acid. It is characterized also by a high coefficient of friction and a crackle or rustling sound when the silk is rubbed on itself.

Going back to the demonstration of "scoop" produced on the skin by the alkyl aryl sulfonates, it will be remembered that after rinsing and drying the skin was considered clean. If the hands are now rinsed with dilute sodium carbonate (less than 0.25%), it is possible to work up a suds again; at the same time the normal feel of the skin is restored and now remains unchanged even after copious rinsing with pure water. The skin, of course, is presumably no cleaner now than before. This suggests that the sensation of an ultra-clean skin surface was produced actually by an adsorbed film of surface-active agent. Incidentally, if the hands are washed with alkyl aryl sulfonate at neutral pH in the presence of sodium sulfate, or at pH 3 to 4 in the presence of organic acid, the "scoop" effect produced is considerably enhanced; in either case, rinsing with dilute alkali restores the normal feel. C-12 alcohol sulfates and alkyl sulfonates of low salt content at neutral pH produce less "scoop" than do the alkyl aryl sulfonates.

At acid pH's, however, the "scoop" is more pronounced although not as fully developed as in the case of alkyl aryl sulfonates under comparable conditions.

The quaternary ammonium compounds produce somewhat different effects. On washing the hands with Alrosept MB (alkyl imidazolinium chloride) or cetyl trimethyl ammonium bromide at pH 7, one becomes acutely aware of the ridges in the palms and fingers; at alkaline pH's mild "scoop" is developed. In either case, after rinsing the hands thoroughly with water, a rinse with dilute acid will produce a very copious suds and the "scoop" will almost disappear—*almost*, because a rinse of normal skin with dilute acid alone will cause a slight increase in friction. With non-ionic surface-active agents "scoop" effects are not marked although adsorption seems to occur to a limited extent as evidenced by slight sudsing after rinsing with water followed by a pH shift to the alkaline side.

In short, the so-called drying or defatting effects of the synthetics may be explained in terms of adsorption phenomenon. Fortunately, the adsorption of surface-active ions by proteins has attracted the considerable attention of textile technologists and biochemists. Work in this field has recently been reviewed by Putnam (2), Valko (3), and Harris (4). Complex formation between surface-active ions and proteins is generally explained in terms of what is called "specific or intrinsic affinity" and electrostatic forces. At its

isoelectric point a protein is considered electrically neutral. At pH's below its isoelectric point, the protein becomes positively charged and cationic in nature; under these conditions it combines with negatively charged colloids in which class are the anionic surface-active agents. At pH's above its isoelectric point the protein becomes negatively charged and anionic in character; under these conditions the protein will combine with positively charged colloids in which class are the cationic surface-active agents. The extent of protein surface-active ion complex formation is determined by hydrogen ion concentration and by electrolyte concentration. Actually, however, solid proteins do adsorb anions at alkaline pH's and cations at acid pH's; this is "explained" in terms of intrinsic affinity of the surface-active ion for the protein.

Neville and Jeanson (5) in 1933 described the adsorption of lauryl sulfate and also Igepon T by wool; at pH 1 the wool adsorbed 25 to 40 per cent of its weight of surface-active anion from a 0.5 per cent solution. As the pH increased the adsorption decreased, although even above the isoelectric point of the wool adsorption is 2 to 3 per cent. Steinhardt, Fugitt, and Harris (6) investigated the adsorption of various anions by wool over the pH range of 1 to 6. While maximum adsorption of dodecyl sulfonic acid was approximately 25 per cent at pH 2, at pH 6 100 gm. of wool would still adsorb 1.2 gm. of anion. It was

also determined that complex formation was reversible, washing the protein with water resulting in the removal of the anion. Steinhardt also concluded from these and other experiments (7) that the affinity of anions for protein increased with molecular weight. Aicken (8) studied the adsorption of primary and secondary alcohol sulfates (molecular weight about 280) by wool. Adsorption was found to increase with increasing acidity to a maximum comparable to the acid binding capacity of the wool—about 80 to 100 milliequivalents per 100 gm. of wool. At neutral pH's per cent adsorption increased with increasing concentration of the solution and was also enhanced by the addition of electrolyte. Attempts to desorb the alcohol sulfate by soaking in water for 48 hours proved unsuccessful, in marked contrast to Steinhardt's results. Finally, reference might be made to the work of King (9) and Neville and Harris (10). The latter confirmed earlier work that wool immersed in neutral soap solution adsorbs sodium ions (cations) faster than it does fatty acid; this was evidenced by a rapid drop in pH of the soap solution. King earlier had analyzed soap solutions in which wool was immersed and had found that sodium ions were adsorbed preferentially and that adsorption of oleate ions or oleic acid increased as the concentration of the solution decreased. This behavior is in marked contrast to the behavior of the highly dissociated neutral synthetic surface-active agents. The

evidence would indicate, therefore, that conditioned as we are to the use of soap, the normal feel of skin is simply that produced by high sodium ion concentration and fatty acid adsorption on the skin surface.

The truth, as some one said, is rarely pure and never simple; the data just reviewed must be considered critically. These studies were all made under conditions approaching equilibrium and with relatively dilute solutions. Equilibrium conditions are possibly not attained in the short shampooing operation and dilute solutions are obtained only during rinsing. The variations in complexity of detergent solutions as a function of concentration are not yet fully appreciated; there is still considerable argument as to whether protein adsorbs large micellar aggregates, surface-active ions, or molecules.

The viewpoint just discussed appears to be, however, of some value in explaining and perhaps indicating the possibility of attacking some troublesome shampoo problems. (1) The rinsing properties of synthetics are undoubtedly affected by their adsorption properties. Anionic agents should rinse better at slightly alkaline pH's; cationics should rinse better at slightly acid pH's. (2) Harshening of the hair, unmanageability, and difficulty in combing after shampooing may very well be the result of increases in friction such as that noted as the result of adsorption of surface-active ions on the skin; adjustment of pH should overcome these difficulties. (3)

Surface-active agents differ in the ease with which they lather on the skin or hair; often several latherings are required. While defoaming by the fatty acids present on the hair and skin is undoubtedly responsible for some of this poor lathering, adsorption of the surface-active agent on the skin would, of course, render this material unavailable for lathering. (4) Salts of surface-active anions and slow rinsing organic bases might be useful in decreasing or eliminating the "scroop" effect. (5) If it is desirable to duplicate the effects produced on the skin and hair by soap, synthetic surface-active agents with carboxylic acid groupings, but with better hard water properties, could be utilized. Materials of this sort have been described and have actually been found to be excellent skin detergents.

Experiments devised to determine the role of conditioning agents, unfortunately, have not been very successful. These materials—added to shampoo detergents to improve softness—are generally non-ionic agents, a typical example being lanolin. Addition of this and other materials to alkyl aryl sulfonates did not appreciably affect the feel produced. There is evidence (11), however, that lecithin (a phospholipoid) and fatty esters of diglycerol do modify the adsorption properties of anionic and cationic agents on cell membranes as they inhibit germicidal activity. Incidentally, it is possible to demonstrate visually the adsorption of quaternary ammo-

nium compounds on glass surfaces (12) by development of rainbow color effects when steam is condensed on the surface; the addition of a wide variety of non-ionic agents did not appreciably affect the development of rainbow color, although the effect of pH was confirmed as in the case of protein adsorption.

The apparent contradiction involved in producing "scroop" on the skin by adsorption of surface-active agents of the type used as lathering agents, and the producing of softness by other surface-active agents, may be resolved as follows: These latter materials are all C₁₈ straight chain compounds. The theory of lubrication as developed years ago indicates that such materials are much better lubricants than the shorter chain compounds of the type used for shampooing. Hydrophilic groups also affect lubricating properties. Aromatic character is also known to affect lubrication adversely. This all corresponds with the observation that alkyl aryl sulfonates and alkyl naphthalene sulfonates produce much harsher feel than straight chain alkyl sulfonates. It was thought that perhaps the feel and frictional properties of the skin might be due to the presence of hydrophilic groupings on the outer side of the surface-active agent film. There is some evidence that this type of arrangement does occur in some cases. However, it has been found that regardless of the type of film which may be on the skin sur-

face, water droplets do not tend to spread readily and the surface of the skin cannot be considered as particularly hydrophilic even when "clean."

There is little question that the work being done on combination of surface-active ions with proteins is of considerable importance and significance to the cosmetic industry. Contributions in this field are appearing at an accelerated rate and while often difficult to follow because of highly mathematical treatments, well deserve the attention of the cosmetic chemist.

Another common misconception is that soap is not suitable for formulation of hard water shampoos. There is no question that soap—especially coconut oil soap—has many desirable properties not easily duplicated by synthetics. Aside from the fact that soap produces the conventional feel of skin and hair, the lather produced by coconut soaps is excellent. It is copious, viscous, and stable in soft water. It rinses readily in soft water. In hard water, the volume and viscosity of the lather fall and during the rinsing operation, the dilution of soap with large quantities of water containing calcium and magnesium results in the precipitation of the corresponding alkali earth soaps on the hair.

The inclusion of water-softening agents in liquid soaps is now widely practiced due to the improved availability of organic sequestering agents which are compatible with potassium and triethanolamine soaps and which do not hydrolyze

on storage in aqueous solutions. Typical of such products is ethylenediamine tetraacetic acid.

The neutral and alkaline salts form chelate complexes with calcium and magnesium (13) and thus prevent the precipitation of soap by these ions. It is now possible to manufacture liquid soaps which often do not require refrigeration or filtering and which will not cloud in glass containers. The addition of a few per cent of ethylenediamine tetraacetate to a soap shampoo will prevent the decrease in lather volume and viscosity in hard water. Foam measurements on dilute solutions of soap and sequestrant have been made (13) and these results have also been confirmed for high concentrations of soap. Five per cent solutions of soap containing 0.5 per cent ethylenediamine tetraacetate show no drop in lather volume or viscosity at 500 ppm. hardness as tested in a Waring blender. This concentration of sequestering agent is also adequate to neutralize such hardness as may be encountered on preliminary dilution and rinsing of the lather. It is not adequate, however, to neutralize the hardness of all the rinse water used, and in all probability these organic sequestrants rinse faster than does the soap, leaving it unprotected.

The precipitation of calcium and magnesium soap on the hair during dilution may be prevented by the addition to the soap of a lime-soap dispersant. The function of this material is perhaps more correctly

to retard the development of soap curds. Table 1 compares the transmittance of 0.2 per cent soap solutions containing 0.02 per cent of various surface-active agents at 25°C. readings being made five minutes after making up the solution.

TABLE 1—TRANSMITTANCE OF 0.2% K COCONATE AND 0.02% DISPERSANT IN 200 PPM. CaCO₃

K coconate only.....	66%
Non-ionic ether.....	85%
Na lauryl sulfate.....	70%
Coconut fatty amide.....	81%
Non-ionic ester.....	84%
Dodecyl toluene sulfonate.....	79%
Oleic amide sulfonate.....	84%

If these solutions are allowed to stand long enough, they will eventually all show the same low transmittance. One cannot, however, formulate soap and lime soap dispersant on the basis of these data alone. The foaming properties of binary mixtures of surface-active agents are not predictable. The adverse effect of soap on alkyl aryl sulfonate foam is well known and has even been utilized to make non-foaming wetting agents. Lathering experiments using high concentrations of soap and alkyl aryl sulfonate confirm the results obtained at low concentrations, although, strangely enough, the defoaming effect is not picked up easily in the Waring blender test. Hand lathering experiments also indicate that the fatty amides of the Alrosol type enhance lather, at the same time retarding precipitation of the

lime soap. None of these materials has the same effect on the lathering properties of the soap in hard water that organic sequestrants have. A mixture of soap, plus lime-soap dispersant, does not show good lathering properties in hard water unless organic sequestrant is present.

Considering the number of years that shampoos have been manufactured and marketed, no one can complain that conditions in this field are static. Shampoos today account for over 50 million dollars in sales volume. The cosmetic chemist today must search constantly for new possibilities. Fortunately, he has an untapped wealth of raw materials still available to draw on.

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