

industrial cleaning applications in a large number of industries. The two main forms in which they are sold as industrial cleaners today are a) 40% active drum-dried flake and b) 50% active triethanolamine neutralized liquid product.

The use of alkylaryl sulfonates in the household detergents began shortly after World War II and was the start of what has proven to be by far their largest use. The three main types of household de-

tergents utilizing these sulfonates are a) spray-dried, heavy-duty detergents for general household laundry, b) spray-dried, light-duty detergents for washing of fine fabrics and dishes, and c) light-duty, liquid detergents for washing of fine fabrics and dishes. Thus, because of their low cost and excellent use properties, they have become the "work-horse" of the synthetic detergent industry.

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## Fatty Alcohol Sulfates

DAVID B. HATCHER, Stepan Chemical Company, Chicago, Illinois

THE FATTY ALCOHOL SULFATES represent an important item of commerce and also are among the earliest detergents to be discovered and introduced. The first alcohol sulfate was prepared by Dumas in 1836. Almost 100 years later, in 1932, the alcohol sulfates were incorporated in the first successful retail detergent in the United States. Now, a quarter century later, they remain of very significant commercial importance.

Since long chain alcohols with carbon chain lengths varying from  $C_6$  to  $C_{22}$  can be derived from various fats and oils, it is necessary to limit the discussion to a few materials which are readily available and of substantial commercial importance. This essentially limits the discussion to the alcohols from four sources, insofar as detergents are concerned, namely: coconut oil, palm kernel oil, tallow, and sperm oil.

For uses other than surface-active agents, castor oil and perhaps other fat-derived alcohols are of some importance, but these by common usage are normally excluded from the category of "fatty alcohol sulfates." The synthetic alcohols, which are beginning to find favor for some use as their ethoxylated derivatives, will not be included in the discussion since they are not fat-derived.

The approximate composition of three of the four fats mentioned above are shown in Table I.

TABLE I  
Fatty Acid Content of Common Fats Used in Fatty Alcohol Production

Usual percentage of fatty acid	Coconut oil	Palm kernel oil	Tallow <sup>a</sup>
Caproic ( $C_6$ ).....	0-0.8	Trace	—
Caprylic ( $C_8$ ).....	5.5-9.5	3-4	—
Capric ( $C_{10}$ ).....	4.5-9.5	3-4	—
Lauric ( $C_{12}$ ).....	44-52	46-52	—
Myristic ( $C_{14}$ ).....	13-19	14-17	6.3
Palmitic ( $C_{16}$ ).....	7.5-10.5	6.5-9	27.4
Stearic ( $C_{18}$ ).....	1-3	1-2.5	14.1
Oleic ( $C_{18}$ ).....	5-8	13-19	49.6
Linoleic ( $C_{18}$ ).....	1.5-2.5	0.5-2	2.5

<sup>a</sup> Bailey—North American Beef Tallow.

The typical lauryl alcohol of commerce as used in the production of lauryl sulfates is the hydrogenated coconut oil type with a portion of the lower boiling and of the higher boiling components removed.

Sperm oil represents a different situation from that of the previous three materials in that the alcohols themselves are derived from sperm oil since they are present in the oil as their esters. A typical saponified sperm oil will yield alcohols (Table II).

TABLE II  
Fatty Alcohol Identity in Sperm Whale Head Oil

	Percentage <sup>a</sup>
Cetyl alcohol.....	50
Palmitoleyl alcohol.....	10-12
Stearyl alcohol.....	10-12
Oleyl alcohol.....	25
$C_{20}$ alcohols.....	Remainder

<sup>a</sup> Of alcohol present.

### Manufacture of Fatty Alcohols

There are moderate quantities of sperm oil alcohols used in this country. Some of these are manufactured domestically, but the large proportion are imported from Europe, where they are obtained by the saponification of sperm oil or spermaceti. In addition to this production by saponification, there are two generally used methods for producing higher fatty alcohols commercially: high-pressure hydrogenation and reduction with metallic sodium.

The choice of methods for producing higher fatty alcohols depends upon many factors which we do not have sufficient space to discuss fully. Briefly the hydrogenation process involves a large capital investment and is limited to producing saturated fatty alcohols since under most conditions of hydrogenation the double bonds are saturated. For some applications unsaturated alcohols, such as oleyl alcohol, are more desirable than the saturated alcohols, and sodium reduction must be used. Hydrogenation is also versatile however in that fatty acids, in addition to the various fatty acid esters, can be used as starting materials. The glyceryl esters are not normally used in this operation since the glycerine is further hydrogenated to propylene glycol and in some cases to isopropyl alcohol. It is more common practice to recover the glycerine from the glyceride first by means of fat splitting or ester interchange. The hydrogenation operation is then carried out, using the fatty acids or the methyl esters. Because of the drastic conditions employed (3,000 to 5,000 psi and 200° to 400°C.) in hydrogenation, there can also be formed an appreciable amount of hydrocarbon, which represents a loss of product yield and can alter the properties of the fatty alcohol derivatives.

The sodium reduction process does not normally represent as large an investment as the hydrogenation method. It is more flexible in that both saturated and unsaturated alcohols can be produced. However, in producing saturated tallow alcohols, for example, the tallow must first be hydrogenated before being

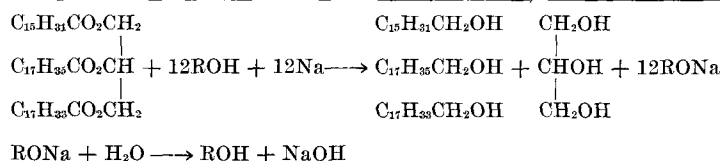


FIG. 1.

### Fatty Alcohols by Sodium Reaction

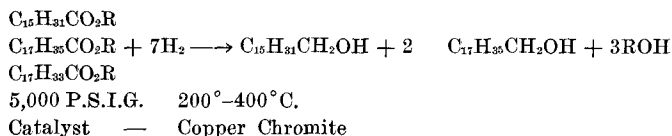


FIG. 2.

reduced with sodium. The starting material must be an ester since fatty acids react directly with sodium to form soaps, giving difficulty in later processing steps. When using the glyceride esters as a raw material, the glycerine is recovered from the process in the form of a caustic and glycerine solution. The usual impurities present in the crude alcohols are soap and unreacted ester, which are later removed through fractional distillation.

These processes are represented in Figures 1 and 2.

### Fatty Alcohols by High Pressure Hydrogenation

Twelve mols of sodium are required to reduce one mole of fat while seven mols (14 atoms) of hydrogen are indicated for the same fat. The extra two hydrogen atoms are needed to reduce the oleic radical so that this becomes stearyl alcohol in the over-all process. There have been catalysts developed which are semi-selective, allowing production of unsaturated alcohols by hydrogenation. However these catalysts require a great lowering in capacity in the plant and are only partially selective so that the practical method of producing unsaturated alcohols is by sodium reduction.

### Manufacture of Fatty Alcohol Sulfates

In view of the great importance of the sulfates it seems worthwhile to examine the method used in producing these materials. A large number of methods have been proposed and used, many of which were specifically for the purpose of sulfating unsaturated alcohols. Processes of this type include:

- sulfating with  $\text{SO}_3$ —dioxane complex;
- sulfating with  $\text{SO}_3$ —pyridine complex;
- use of potassium or sodium chlorosulfonate;
- sulfation with sulfuric acid and urea or chlorosulfonic acid plus urea or other lower fatty acid amide;
- sulfation with  $\text{SO}_3$ —sodium nitrite complex.

These processes are currently commercially unimportant, and more generally applicable methods are used for the bulk of the alcohol sulfates being produced today. These processes include sulfation with sulfur trioxide, sulfation with sulfuric acid, sulfation with chlorosulfonic acid, sulfation with sulfamic acid, and sulfation with ammonium and amine sulfates.

The reactions involved in these processes are set forth in Figure 3.

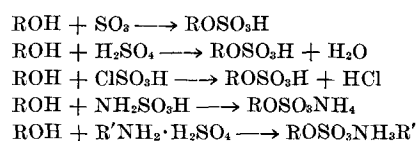


FIG. 3

Recently there has been very active interest in developing a process for the use of sulfur trioxide in sulfation of alcohols. The process which seems to have been the most successful involves the introduction of  $\text{SO}_3$  into the alcohol as the vapor in a stream of dry air or nitrogen.

The use of sulfuric acid also is reported to be quite extensive although the degree of sulfation is lower than with some other types of sulfation. This is not necessarily a disadvantage where coconut types are being sulfated for use in heavy-duty detergents since certain patents report the addition of small percentages of unsulfated alcohol to heavy-duty formulations to be advantageous.

Chlorosulfonic acid also enjoys some commercial usage in the production of alcohol sulfates. It yields a high degree of sulfation, but the acid itself and the hydrogen chloride produced are both extremely corrosive and must be handled in corrosion-resistant equipment which lends itself to this type of usage.

Sulfamic acid and the ammonium-amine sulfates are used where the ammonium or amine sulfate is required.

In general, the sulfation of alcohols is somewhat more difficult than the sulfonation of alkyl benzenes. This is due to the tendency of alkyl sulfuric acids to hydrolyze back to the alcohols and sulfuric acid. This hydrolysis is arrested upon neutralization of the so-called "sour oil," and the resulting product is very stable in alkaline solutions.

### Properties of Fatty Alcohol Sulfates

The properties of the various alcohol sulfates of course vary with chain length just as in other series. The lower molecular weights are wetting agents. As the chain length increases up to 12, they become very important detergents and excellent foamers. As the chain length increases farther, the solubility and foaming decrease and emulsifying properties increase.

In addition to generalities, certain specific proper-

ties of the alcohol sulfates are of interest. First, the lauryl sulfates are extremely good foamers, not only with regard to the quantity of the foam but from the standpoint of character of the foam. The lauryl sulfate foam has the appearance of fine, small bubbles which give a very white and rich appearance. It is this property as much as its ability to give clean lustrous hair when properly formulated that contributes to its use in shampoos.

Another interesting property of lauryl sulfates is their change in viscosity with change in salt content. Sodium lauryl sulfates that are fluids can be changed to heavy pastes by the addition of sodium chloride or sodium sulfate. This property gives to a cosmetic formulator, a control over the viscosity of his product which is difficult to obtain and maintain with other products.

The alkyl sulfate salts also exhibit a reversed solubility when compared with soaps. The magnesium salt is more water-soluble than the sodium salt, and the potassium lauryl sulfate exhibits only a limited solubility in water.

Other properties will be discussed along with the uses involved.

#### Uses of Fatty Alcohol Sulfates

**Cotton Detergents.** The largest use of fatty alcohol sulfates has been and is in detergent powders. They are very fine cotton detergents when built with phosphates. The coconut oil types predominated in this use for many years but recently have been replaced partially by tallow alcohol sulfates. These also are excellent cotton detergents but, in contrast to lauryl sulfates, are low foamers. This handicap is overcome by using mixtures of the fatty alcohol sulfate with lauryl sulfates or dodecyl benzene sulfonates to supply the foam. A disadvantage of these products is cost. They are more expensive on a per pound basis than alkyl aryl sulfonates.

For use as heavy-duty, cotton detergents the sodium alcohol sulfates are blended with alkaline salts, such as sodium tripolyphosphate, tetrasodium pyrophosphate, sodium silicate, and carboxymethyl cellulose. Optical dyes and foam stabilizers are also included in these formulations. In some cases other detergents, such as alkyl aryl sulfonates, are blended with the alcohol sulfates. Both coconut and tallow alcohols are used for this application, and the ratio used depends upon the amount of foam which is desired, the coconut alcohol sulfate producing a more copious foam at low temperatures than the more insoluble, tallow alcohol sulfate. Essentially the same principle applies as in the case of coconut tallow soap blends. A mixture of equal parts of coconut alcohol sulfate and tallow alcohol sulfate yields a product with outstanding foaming and detergent characteristics at a cost below that which would apply if coconut types alone were used.

Figure 4 indicates the results of testing three heavy-duty detergent formulae. It will be noted that the inclusion of fatty alcohol sulfates in the formulae resulted in greatly improved detergency although on a cost-performance basis it would seem likely that formula C is the best of the three. This formulation, employing both alkyl aryl sulfonate and fatty alcohol sulfates, offers excellent detergency as well as satisfactory foam characteristics. This formulation is a typical "screening" formula used for evaluating or-

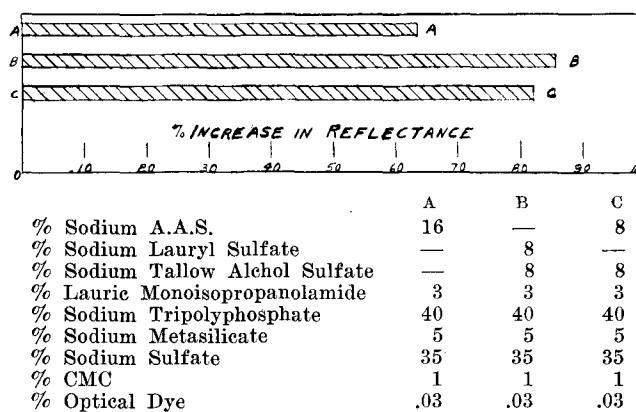


Fig. 4. Cotton detergency of built fatty alcohol sulfates  
50 p.p.m. hardness, 120°F., 0.25% solids conc.

ganic actives and would require some modification before it would prove entirely acceptable in a household package. Two obvious modifications would be to increase the sodium tripolyphosphate content to 50% and to reduce the pH by using silicates other than the metasilicate.

**Liquid Dishwashing.** The middle cut of alcohols derived from coconut oil, so-called "lauryl alcohol," has been sold for many years as the sulfate for dishwashing. It proved very successful as the powder and later was introduced as the major component of a retail liquid dishwashing compound. This was and is sold in considerable volume although it has been replaced as the number one liquid dishwashing product. The fatty alcohol sulfates are excellent for dishwashing detergent, but again their major disadvantage is cost.

**Shampoo Ingredients.** Most of the largest selling shampoos manufactured in the United States are based on lauryl sulfate. Various salts are used, such as magnesium, sodium, ammonium, or ethanolamine lauryl sulfates, to obtain various properties. Two typical basic formulas are as follows.

#### Cream Shampoo

60% Sodium lauryl sulfate paste (30% active)  
6% Sodium stearate  
1% Cetyl or stearyl alcohol  
33% Water  
Perfume

#### Clear Liquid Shampoo

94% Triethanolamine lauryl sulfate (40% active)  
4% Propylene glycol  
2% Oleic monoethanolamine  
Dilute to 26% lauryl sulfate active and perfume

To these basic formulae are added magnesium stearate for a pearl effect, glyceryl or sorbitol stearate for thickening, fatty acid amides for foam stability, and other additives for emolliency and special effects.

This use in shampoos is very widespread. In fact, detergent shampoos on the American market which are not based on alcohol sulfates are few in number. The major reasons for this popularity with shampoo manufacturers is based on the fine foaming characteristics of lauryl sulfates and their resistance to the defoaming action of soils commonly encountered on hair. They yield an excellent "first suds," which is

necessary for any shampoo if it is to obtain and hold any significant portion of the market.

*Textile Auxiliaries.* The fatty alcohol sulfates are not widely used as textile auxiliaries but are used in some places for kier-boiling of cotton. The  $C_4$ - $C_{10}$  alcohol sulfates are sometimes used as wetting agents in the mercerizing of cotton. The alcohol sulfates are used as levelling and suspending agents in the dyeing of mixed wool and acetate rayon fabrics.

*Electroplating.* The alcohol sulfates are used in electroplating. In nickel plating baths they reduce the crystal size of the nickel plated on the metal; consequently the porosity of the film is reduced.

*Ulcer Remedies.* The decyl and lauryl sulfates are used for treatment of stomach ulcers. The exact reason for their effectiveness is not known, but tests have indicated their usefulness.

*Toothpastes.* Lauryl sulfates for use in toothpaste have long been known to be very effective and advantageous. The foaming characteristics and clean feel left in the mouth are their main reasons for use.

*Rug and Upholstery Cleaners.* The sodium lauryl sulfates are widely used for on-location rug and upholstery cleaning. Their detergency properties are excellent for this purpose, yet they do not wet through the rug or upholstery, which would often cause mildew. The sodium salt is used so that it can be picked up by a vacuum cleaner after the item is dry. Where detergents are used which are not dry powders when

dehydrated, the detergents themselves cause rapid resoiling of the item cleaned.

*Miscellaneous Uses.* The fatty alcohol sulfates are also used in alkaline metal cleaning baths, in detergent bars, and as emollients and emulsifiers for cosmetics. Combinations of alcohol and alcohol sulfates or  $C_{16}$ - $C_{18}$  chain length yield stiff, stable emulsions for creams and similar preparations. An example of this is the use of cetyl alcohol in a cream brilliantine formula.

The lauryl sulfates are used for washing the felts used on paper machines. Surprisingly this same detergent has been shown to be effective against aphids and soft-bodied insects.

A recent patent indicates that hexyl sulfate is useful as a coupling agent for higher alkyl sulfates in liquid, heavy-duty detergent formulations.

The list could continue as the alcohol sulfates have found wide and varying usage. However there is one derivative of the fatty alcohols which should be mentioned, even though not alcohol sulfates but the fatty alcohol ether sulfates. These materials are just being introduced in the American market and are prepared from fatty alcohols by addition of ethylene oxide, followed by sulfation. They have many of the good properties of the fatty alcohol sulfates yet allow for greater variation in their properties through change in the length of the ether chain between the alkyl radical and the sulfate.

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## The Alkylolamides

JEROME KRITCHEVSKY, Ninol Laboratories, Chicago, Illinois

AS WITH SO MANY DISCOVERIES, the Ninol alkylolamides originated as a by-product of an entirely different line of investigation. Sometime in the late '20's Wolf Kritchevsky began a study of methods for transforming water-soluble dyestuffs into oil-soluble types and observed that acidic dyes containing carboxyl groups could be precipitated by basic dyes containing amine groups. By then treating water-soluble acid dyes with various amines, he found that esters made from alkylolamines and fatty acids, such as oleyl ethanolamine, could convert water-soluble dyes to oil-soluble types.

In the course of preparing these ester amines Dr. Kritchevsky made a significant observation. He noted that, by heating one mole of coconut fatty acid with one mole of diethanolamine, a water-insoluble condensate was produced as expected; surprisingly however, the presence of an extra mole of diethanolamine seemed to modify the reaction to give a product completely soluble in water. This new material foamed and wetted well and showed good resistance to hard water. Recognizing the importance of this development, Dr. Kritchevsky filed patent applications, which resulted eventually in issuance of U. S. Patent 2,089,212 in 1937, covering what has been described as the first American detergent.

### Chemistry

In spite of the great commercial importance these alkylolamides (referred to as the "2:1 Type") have

since achieved, their chemistry has never been fully elucidated. It is known that merely mixing an extra mole of diethanolamine (DEA) at room temperature with a 1:1 coconut diethanolamide will not impart water solubility since heating for several hours at about 140-150°C. is required.

U. S. Patent 2,089,212 speculates that the first mole of diethanolamine reacts with the coconut fatty acid during heating to form an amide, and the second mole of DEA then reacts further with a terminal hydroxyl to form a quaternary ammonium compound. This is not too probable however, in view of the fact that the alkylolamides do not exhibit definite cationic behavior and are not as highly alkaline as a quaternary base would have to be.

Furthermore the fact that the second mole of DEA is so weakly held that it can be titrated or distilled off would indicate it is physically rather than chemically combined. One possibility might be that the second mole of DEA is hydrogen-bonded to the diethanolamide in some way, thus imparting water solubility to the otherwise sparingly soluble amide.

Although these water-soluble coconut alkylolamides have become the most important type commercially, derivatives made from other fatty acids and two moles of DEA have also been used quite extensively in cosmetics, textiles, and other applications. In addition, alkylolamides of a simpler type, made by reacting equimolar quantities of fatty acids and monoalkylolamines, such as monoethanolamine or isopropanola-