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Properties and Uses of Some Unsaturated Fatty Alcohols and Their Derivatives

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ABSTRACT

A number of unsaturated fatty alcohols are known, but only those of the C_{16} and C_{18} chain lengths are of much importance. In particular, oleyl alcohol, 9,10-octadecenol-1, is by far the most important. A variety of grades of oleyl alcohols is produced and used in the USA ranging from high purity material having iodine values (IV) of 90-95 to those having IV of 45-55, with the other components being primarily cetyl (hexadecanol-1) and stearyl (octadecanol-1) alcohols. This paper takes a brief look at the various grades of unsaturated alcohols used in the USA, methods of preparation, and the change in physical and chemical properties as the octadecanol-1 content and IV decline. Uses of these alcohols industrially and in cosmetic and pharmaceutical preparations are also discussed. Unsaturated alcohols are useful chemical intermediates since they have two reactive sites, the hydroxyl group and the carbon-carbon double bond. Particular attention is paid to the properties, uses and potential uses of some of their sulfates, ether sulfates, ethylene oxide adducts and ethylene/propylene oxide adducts as detergents and emulsifiers for ultimate use in cosmetics and light-duty and heavy-duty systems. Current estimated consumption of unsaturated alcohols in the USA is discussed.

INTRODUCTION

The best known of the unsaturated fatty alcohols is oleyl alcohol (9-octadecenol-1), although palmitoleyl (9-hexadecenol-1) and myristoleyl (9-tetradecenol-1) are also well known. The latter two, however, are encountered in such small quantities that they are never isolated, and are usually viewed merely as other unsaturated alcohols in an alcohol mixture in which the major component is oleyl alcohol.

Reactions of the unsaturated fatty alcohols at the hydroxyl group are similar to those of the saturated alcohols. The double bond(s) in these alcohols, however, are other reactive sites. As a result, they are subject to side reactions which are frequently undesirable and difficult to control. Derivatives which are dark in color and have a bad odor may result when these compounds are subjected to ammonolysis or esterification. If attempts are made to sulfate these unsaturated alcohols, sulfation or sulfonation tends to occur at the double bond in addition to sulfation at the hydroxyl group unless special precautions are taken. In general, unsaturated alcohols are more expensive than saturated alcohols because of additional processing costs required to protect the double bond.

For these reasons, uses of unsaturated alcohols have been restricted to specialized applications. The influence of the double bond in these unsaturated alcohols, particularly on the physical and performance properties of some of their derivatives, has been largely overlooked or ignored, if recognized at all. Today, mainly because of changing consumer demand, environmental requirements, energy conservation needs and increasing petroleum and ethylene feedstock costs, this picture is beginning to change.

TYPES OF UNSATURATED ALCOHOLS

The major unsaturated alcohol is oleyl alcohol. The pure compound has the physical and chemical properties shown in Table I.

Pure octadecenol-1 is not available commercially. However, in the USA there are various grades of unsaturated fatty alcohols. They are generally called oleyl alcohols if they contain at least 55% oleyl alcohol and have an iodine value (IV) of 65 or higher. These are classified as refined, technical or industrial grade oleyl alcohols. They are characterized for specification purposes by hydroxyl number, iodine value, acid number, saponification number, cloud point, color and odor. Usually the hydroxyl value, iodine value and cloud point data are the main factors used to judge the quality of an oleyl alcohol.

Broadly, these classes of oleyl alcohols will compare as shown in Table II. Slight variations may occur depending on the producer.

In general, the higher the IV and the lower the cloud point (usually below 5 C), the higher the oleyl alcohol content. A rise in cloud point and decline in IV indicate increased saturated alcohol content. These saturated alcohols are usually stearyl and cetyl alcohols. The cloud point is also increased if the ester content is increased to above 1-2% or if C_{16}-C_{18} hydrocarbons are present in

TABLE I

Properties of Oleyl Alcohol

Structural formula	$CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_2OH$
Molecular weight	268.47
Iodine value	94.5
Hydroxyl value	209.0
Melting point (C)	-7.5 (1)

TABLE II

Commercial Classes of Oleyl Alcohols

Type of oleyl alcohol	Hydroxyl value	Iodine value	AOCS cloud point (C)
Refined	205-215	85-95	< 10
Technical	205-220	80-90	< 15
Industrial	205-225	65-75	< 28

appreciable quantities such as greater than 1-2%. This is why, in the refined oleyl alcohols, the saponification number will be no more than 1.5 but frequently below that. The quality of an oleyl alcohol can be frequently judged by its wet chemical analysis. It is important to note, however, that a high IV is not a true measure of the oleyl alcohol content in a product and its composition can only be determined by gas liquid chromatography (GLC).

As an example, two essentially odorless and colorless refined oleyl alcohols were checked by wet chemical analyses in the Sherex laboratories, as shown in the top half of Table III. Based on these data, one would conclude that both products were of excellent quality and suitable for cosmetic use. When used in typical cosmetic formulations for creams and lotions, no performance differences were detected. From these analyses one would also tend to conclude that there were only small differences between these two samples and that their compositions were similar.

When these same samples were analyzed by GLC, however, the compositions shown in the bottom half of Table III were obtained. Note that sample 1 has a lower oleyl alcohol content but contains a significant amount of linoleyl alcohol, whereas sample 2 contains a higher concentration of oleyl alcohol, no polyunsaturated alcohols, and a somewhat higher C_{20-1} level. The total amount of unsaturated alcohols in both samples is approximately the same. The carbon chain lengths of saturated alcohols range from C_{14} to C_{20} and the overall distributions are similar, except that sample 2 contains 2.44% C_{20} alcohols whereas sample 1 contains only 0.14%. All of the monounsaturated alcohols are of the *cis* variety and the linoleyl alcohol is the C_9 *cis*, C_{12} *cis* species. This information indicates that the raw material source is critical to the composition of the finished alcohol. Processing techniques may also be a factor.

One other alcohol that contains a significant amount of oleyl alcohol, although by the earlier definitions would not be classified as an oleyl alcohol, is tallow alcohol. It has the typical composition shown in Table IV. The typical wet chemical analysis shows tallow alcohol to have an acid value of 1.0, a hydroxyl value of 215, iodine value of 52, saponification value of 2.0 and a cloud point of 35 C. Tallow alcohol is produced from tallow acids or their methyl esters. Sherex believes that this type of fatty alcohol, particularly its alkoxylates, is going to become of significant industrial importance during the next decade.

RAW MATERIAL SOURCES FOR OLEYL ALCOHOLS

Until 1973, in the USA and throughout most of the world, the primary source of oleyl alcohol was sperm oil. In that year, the US federal government declared the sperm whale to be a member of an endangered species and sperm oil or its derivatives could no longer be processed or used in the USA. Since then, many nations have followed suit, so that today in the USA and Western Europe these unsaturated fatty alcohols are derived from other natural fats and oils.

TABLE III

Wet Analyses of Two Commercial Oleyl Alcohols

	Sample 1	Sample 2
Property by wet analyses		
Iodine value	95.0	86.5
Hydroxyl value	210.9	208.1
Acid value	0.9	0.1
Saponification value	1.2	0.6
Cloud point (C)	1.34	-1.0

Unsaturated alcohols	Weight, %	
	Sample 1	Sample 2
Compositions by GLC		
C_{14-1}	0.74	0.43
C_{16-1}	9.14	7.94
C_{18-1}	65.05	77.72
C_{18-2}	12.78	—
C_{20-1}	0.49	2.68
Saturated alcohols	11.80	11.23

TABLE IV

Composition of Tallow Alcohol

Alcohol	Weight, %
C_{12}	1
C_{14}	4
C_{16}	23
C_{16-1}	4
C_{18}	23
C_{18-1}	41
C_{18-2}	3
C_{20}	1

The oleyl alcohols are made from oleic acid or one of its esters, usually the methyl ester (2).

The oleic acid is usually derived from tallow, which contains 43-45% oleic acid and 1-5% linoleic acid, and olive oil which contains 61-63% oleic acid and 16-20% linoleic acid. Of more recent interest in the USA as a source of oleic acid is canola oil from Canada. This oil contains ca. 60% oleic acid, 20% linoleic acid and 10% linolenic acid (3). Palm oil may also be used since it contains 38-42% oleic and 10-12% linoleic acid. Tall oil containing ca. 60% oleic acid and 38% linoleic acid may also be used.

PREPARATION OF OLEYL ALCOHOL

If the product is to be made from the methyl ester of oleic acid, the simplified reaction may be represented as:

$$\mathrm{RCOOCH_3 + 4\,[H] \rightleftarrows RCH_2OH + CH_3OH}$$

The reaction will be run at 3500-4200 psi at 300-350 C using suitable catalysts (4).

When the product is made under similar reaction conditions from oleic acid, the reaction may be represented simply as:

$$\mathrm{RCOOH + 4\,[H] \rightleftarrows RCH_2OH + H_2O}$$

The reaction from oleic acid is somewhat more complicated than as represented above, intermediate oleyl oleate forms and is eventually reduced to oleyl alcohol and water (5).

USES OF OLEYL ALCOHOLS

The refined oleyl alcohols are used primarily in cosmetic and pharmaceutical preparations where advantage is taken of their light color, low odor and fluidity. They are used as the free alcohol in creams and lotions in which they function as emollients and emulsion stabilizers. The concentrations used in such emulsions are low, usually 1.0-4.0% by weight of the finished product. The oleyl alcohol imparts a smooth, silky feel to the skin. It shows a primary skin irritation index of 1.33 and has an LD50 above 25 g/kg and is therefore considered nonirritating to the skin and nontoxic (6).

The technical grade of oleyl alcohol is also sometimes used in cosmetic emulsions since it also has good color and low odor. It is most likely to be used as a chemical intermediate for the preparation of surface-active agents such as ethoxylates, sulfates and esters.

The 2-, 10- and 20-mole ethoxylates have long been used by the cosmetic industry. The 2-mole adduct is used primarily as an emollient and emulsion stabilizer in creams and lotions, whereas the 10-mole adduct is mainly used as an emulsifier and the 20-mole adduct functions as a solubilizer and humectant.

The direct sulfation of oleyl alcohol using conventional sulfating reagents such as SO_3 or $ClSO_3H$ without attack of the double bond is difficult and the resulting products are usually dark in color. Sulfation with SO_3 dioxane complexes, SO_3 pyridine complexes and sulfamic acid have been reported, but removal of pyridine and dioxane is difficult and costly. The sulfamic system is slow and reaction time long, because when the reaction is run in the absence of a solvent, the viscosity of the reaction mass is high and difficult to control.

A Japanese patent (7), describes an interesting method for the manufacture of sulfuric acid esters of aliphatic unsaturated alcohols. The process essentially involves continuously contacting a thin film stream of the unsaturated alcohol with a gas stream of SO_3 diluted with an inert gas, such as nitrogen or air, in which the concentration of the SO_3 is 2-15% volume of the gas stream. The SO_3/alcohol molar ratio is maintained at 0.95-1.15 and the reaction temperature is between 70 and 150 C. The reaction temperatures appear to be high when compared to those normally used for batch sulfation. However the contact time, although none was reported, would be short, and the intermediate sulfuric acid ester was immediately stripped of gases and immediately neutralized with a slight excess of 10% NaOH solution.

In one series, the authors report that the molar ratio of SO_3 to oleyl alcohol was held at 1.05. The starting alcohol had a hydroxyl value of 210 and an IV of 83. They report the results shown in Table V. The percentage conversion was calculated from the unreacted alcohol. The percentage of double bonds remaining was determined from the IV of the sulfated material compared with the theoretical value, had no double bond attack occurred.

The authors report that sulfates with high IV have good solubility in water and are light in color. They are reported to have good detergency for clothes washing and are easily rinsed and make the washed fabric feel pleasant to the touch. They are reported to be particularly useful in liquid household detergents.

TABLE V

Sulfation of Oleyl Alcohol

Sulfation temperature (C)	90	120	150
Alcohol sulfated (%)	92	93	91
Double bonds remaining (%)	95	97	92

The industrial grades of oleyl alcohol and their derivatives are widely used in lubricants and as petroleum additives. When the oleyl alcohols are sulfurized at the double bond, they become extreme pressure additives for lubricating oils and cutting oils. The esters of oleyl alcohol such as oleyl oleate have properties similar to sperm oil. Oleyl esters of dicarboxylic acids such as maleic and succinic acid have been used as lubricants and plasticizers. The oleyl alcohols are used as cosolvents and plasticizers in printing inks. They are also used in the textile industry as fiber lubricants and modifiers for fiber lubricant systems. They are also used as defoaming agents.

VOLUMES OF UNSATURATED FATTY ALCOHOLS

There are no published figures for the annual volumes of the C_{16}-C_{18} unsaturated alcohols produced and sold. It is our judgement that US and Western Europe consumption combined is probably under 50 million lb/year with Western Europe using considerably more than the USA. The major portion is used for industrial applications.

Energy conservation and economic trends, as far as raw material costs and changing finished product performance requirements for formulated detergent products will have a significant effect on raw material feedstocks for surfactants in the USA and Canada during the next decade. The nature of these trends and changing finished product requirements are what causes Sherex to view the future for C_{16}-C_{18} fatty alcohols from fats and oils optimistically, and to anticipate increasing importance for unsaturated alcohols usch as tallow alcohol described earlier.

Vogel has pointed out that synthetic alcohol processes require 8 times as much energy to produce a pound of fatty alcohol than that required to produce a pound of natural alcohol from triglycerides. Ethylene prices in the USA are expected to increase as natural gas deregulation is completed by 1986. These prices could increase by as much as 20% per year through 1986; and 70% of the ethylene used in the USA comes from natural gas.

Based on the base model, it is apparent that the cost-index projection for synthetic alcohol processes will be higher than those of linear alkylbenzene sulfonates (LAS) and natural alcohol economics through 1992. Vogel also points out that the Conoco affiliate, Condea, has produced detergent range alcohol from triglycerides, and that Conoco completed the engineering study for a natural alcohol plant based on fatty acids.

A similar message comes from Buchold (5) who points out the better economics in producing fatty alcohols from triglycerides and emphasizes that the triglycerides are a renewable raw material source.

We concur with these observations and further believe the C_{16}-C_{18} alcohols, both saturated and unsaturated, derived from tallow will show the least cost increase and become more and more competitive with the coco range alcohols, in part because of price fluctuations for coconut oil and because of increasing costs of synthetic alcohols.

An energy-saving trend which has become very pronounced in the USA is the lowering of the washing and rinsing temperatures for laundering clothes. Fifteen to 20 years ago, it was standard practice to wash clothes at 60 C or higher. All detergency tests in laboratories for the evaluation of surfactants were conducted at this temperature. The rinse water was not much cooler. As the energy crisis struck, machine designs for new washers were changed so that the warmest water used is 50 C, with the ability to change the temperature setting on the machine so that the wash water is 40, 30 or even 20 C. Laboratory detergency tests have been modified accordingly. This development has also led to the development of the so-called cold-water detergents.

Another recent development in the USA is the popularity of the heavy-duty liquid detergents. Today they hold 22-25% of the US consumer heavy-duty laundry detergent market and are growing in popularity. These products usually contain 30-40% surfactant and the surfactant system comprises nonionic and anionic surfactants. The ratio of nonionic to anionic is usually 3:1 (Table VI).

The most common nonionics used are made from saturated coco range fatty alcohols containing ca. 60% ethylene oxide. The most commonly found anionic is the sodium salt of linear alkylbenzene sulfonic acid, although in some cases a coco ether sulfate or tallow ether sulfate may be found.

These heavy-duty liquids must be clear and uniform at room temperature and remain so on the store shelf. They must have low cloud points, at least down to 5 C or lower, and remain fluid at this temperature. If frozen, they must return to their original form, clarity and appearance by simply standing at room temperature without agitation.

In 1968, a patent (9) was issued that showed that it is possible to make liquid nonionic detergent from saturated or unsaturated fatty alcohols which are mixed alkoxides of ethylene oxide and propylene oxide, providing the two oxides are uniformly mixed together prior to the alkoxylation. Under these conditions the two oxides are randomly added to the alcohol, resulting in products that are liquid at 20 C or lower providing the molar ratio of ethylene oxide to propylene oxide was between 2:1 and 4.5:1.

If comparisons are made between four adducts (Table VII) made from tallow alcohol and hydrogenated tallow alcohol, significant differences are seen in the physical properties. Adducts were made containing a total of 14 and 16 moles of alkoxides in which the molar ratio of ethylene oxide to propylene oxide was held constant at 3:1. The carbon chain length distribution for both alcohols was the same, except that the hydrogenated tallow alcohol contained essentially no unsaturation having an IV of less than 0.5.

If straight ethylene oxide adducts are made from both alcohols having 14 and 16 moles of ethylene oxide, waxy solids result, with freezing points in the 33-40 C range. When similar adducts are made from technical oleyl alcohol with IV of ca. 80, the freezing point is ca. -5 C. The surface and interfacial tensions at 0.025% concentration in water were determined in dyne/cm by the ASTM D-1331-56 standard method. The results are also shown in Table VII. The surface tension of water at 25 C is 72 dyne/cm. The interfacial tension of water against Nujol (refined mineral oil) at 25 C is 32 dyne/cm.

TABLE VI

Formulation for 30% Active Heavy-Duty Liquid Detergent

	Percentage
Nonionic	22.5
NaLAS	7.5
Triethanolamine	2-6
Ethanol	2-6
Inorganic salts	2-4
Water	Balance
Color, perfume, optical brightener	To suit

TABLE VII

Solidification Points of Four Tallow Alcohol Adducts

	Tallow alcohol		Hydrogenated tallow alcohol	
	14 EO/PO	16 EO/PO	14 EO/PO	16 EO/PO
Solidification point (C)	4-6	2-4	16-18	18-20
Surface tension, 25 C	34.4	35.4	35.5	36.00
Interfacial tension (Nujol), 25 C	7.3	7.2	8.0	7.90

These adducts are moderate to low foamers showing Ross-Miles foam heights or 50-75 min at the 0.025% concentration in water at 25 C. Their foaming is not significantly lowered by hard water showing declines in foam heights of only 3-5 min even in 300 ppm hard water. These ethylene oxide/propylene oxide adducts will disperse readily in cold water with minimal agitation. An outstanding feature of those derived from tallow alcohol is that they do not gel when they are dispersed in cold water, regardless of the concentration. Those derived from hydrogenated tallow alcohol give fluid dispersions until the concentration in water reaches the 50% level. At concentrations above this, gels tend to form until the concentration goes well above 90%.

Because of these properties, it is obvious that the ethylene oxide/propylene oxide adducts derived from tallow alcohol offer a number of economic advantages. They are liquids at room temperature and are therefore easy to handle and do not require heating before formulation. They disperse readily in cold water and no energy input is required for their solution. The fact that they do not form gels in water at any concentration allows for the preparation of highly concentrated liquid detergents, thus saving on packaging, transportation and formulation costs. The relatively minor change in freezing point in using technical oleyl alcohols as the hydrophobe, instead of tallow alcohol, is not worth the cost.

Ethylene oxide (EO)/propylene oxide (PO) adducts of tallow alcohol were prepared in which the molar ratio of EO to PO was held constant at 3:1. The products made contained 10.5, 13.0 and 14.0 total moles of alkoxide. Also prepared were the 9-, 11-, and 14-mole ethylene oxide adducts of tallow alcohol. All showed similar surface activity and foaming properties to the four EO/PO adducts previously described. These adducts were evaluated in a standard heavy-duty liquid detergent formulation shown in Table VIII.

For comparison, the same formulation was made in which the nonionic was Neodol 25-7 which is a 7-mole ethylene oxide adduct of Neodol 25 which is a saturated C_{12}-C_{15} alcohol with ca. 25% methyl branching.

TABLE VIII

Standard Heavy-Duty Liquid Detergent Formulation

Component	Weight, %
Nonionic	22.5
NaLAS	7.5
Triethanolamine	2.0
Ethanol	5.0
KCl	2.0
Water	61.0

The 4 systems were all clear and fluid at room temperature, and all remained clear and fluid at 4.4 C. It is interesting to note that when similar systems were made using nonionics from the same tallow alcohol but containing 9, 11 and 14 moles of ethylene oxide only, all systems were gels at 4.4 C and became cloudy at ca. 10 C. The straight tallow alcohol ethylene oxide adducts also tend to form gels when added to water, and therefore require some heating as well as stirring for rapid dispersion. These properties of the straight ethoxylates of tallow alcohol make them somewhat less suitable for heavy-duty liquid detergents unless more coupling agent, such as ethanol, is used. This is certainly not true from a detergency standpoint, as will be observed in the detergency data.

The procedure for detergency evaluation employed the Terg-O-Tometer made by the United States Testing Company, Inc., of Hoboken, New Jersey. Twelve 3 in. by 4 in. swatches, six of each fabric used, were washed in 1,000 mL of water to which had been added 1.0 g of formulated product so that the active detergent concentration was 0.03%. The fabrics and soil used were 50% permanent press cotton polyester, 35% cotton, with Spangler soil (synthetic sebum and air conditioner dust made by Scientific Services of Oakland, New Jersey), and 50% permanent press polyester, 50% cotton with carbon black, mineral oil and vegetable oil made by the United States Testing Company, Inc., of Hoboken, New Jersey. The swatches were washed for 10 min at 29 C in 140 ppm hard water at 100 rpm agitator speed. They were rinsed for 5 min at the same temperature and agitation speed in water of the same hardness. The dried fabric was evaluated using a Photo-Volt reflection and glossmeter 670 using the y search unit with tristimulus filter and the average percentage soil removal calculated from these data. (The Photo-Volt unit is made by Photo-Volt, Inc., of New York.) The data from the first series are shown in Table IX.

None of the tallow alcohol alkoxides performed quite as well by this test at this washing temperature. It appears that 13.0 or 14.0 moles of ethylene oxide and propylene oxide are too much for this type of system and it is suggested that even 10.5 total moles is too much.

In a second series, the test was repeated using the same standard formulation for two of the three using as the anionic NaLAS and Neodol 25-7 and NaLAS with the tallow alcohol adduct having 10.5 total moles of ethylene oxide and propylene oxide. In the third of this series, the NaLAS was replaced with an equal amount of Na-hydrogenated tallow alcohol ether sulfate in which the tallow alcohol was first ethoxylated with 6 moles of ethylene oxide and formulated with the 10.5-mole adduct of tallow alcohol. The same detergency tests under the same conditions were run. The results are also shown in Table IX.

Obvious good reproduction of the results were obtained when the first two systems were rechecked. A distinct improvement in detergency resulted, however, when the hydrogenated tallow ether sulfate was used with the 10.5-mole adduct of tallow alcohol instead of NaLAS.

Even though the straight ethylene oxide adducts of tallow alcohol were somewhat disappointing when used in the base formulation in that they clouded at ca. 50 C and gelled at 4.4 C, their detergent properties were evaluated. Again the same base formulation was used as in the first series and the same detergency test used for evaluation.

These results on series 3 in Table IX indicate that more than 9.0 moles of ethylene oxide on tallow alcohol are needed and that the 11.0- or perhaps the 12.0-mole adduct may be optimum for these washing conditions. Although some formulation problems may exist for the liquid systems, these products are certainly suitable for powdered detergents.

It is also interesting to note that no change in performance of the 11-mole ethylene oxide adduct was observed when Na tallow ether sulfate was substituted for the LAS and the detergency tests repeated using the 11 mole EO adduct of tallow alcohol. The results from this fourth series are also shown in Table IX. Important here is the fact that systems containing the 11-mole tallow alcohol ethylene oxide adduct are now giving better detergency than those based on the Neodol 25-7.

A series of 50% active detergent formulations was prepared and studied for their clarity and gel properties at low temperatures. The nonionics used were Neodol 25-7 and the 10.5-, 13.0- and 14-mole ethylene oxide/propylene oxide adducts of tallow alcohol. The basic formulation used is shown in Table X. All systems were clear and fluid below 4.4 C.

Another series of 30% detergents was made in which no ethanol was used as a coupling solvent or hydrotrope.

TABLE IX

Detergency Tests with Heavy-Duty Liquid Detergents

	Soil removal (%)
Nonionic used in series 1	
Neodol 25-7	70.0
Tallow alcohol + 10.5 EO/PO	68.0
Tallow alcohol + 13.0 EO/PO	63.0
Tallow alcohol + 14.0 EO/PO	63.7
Anionic-nonionic used in series 2	
NaLAS Neodol 25-7	70.7
NaLAS Tallow alcohol + 10.5 EO/PO	68.0
NaTES Tallow alcohol + 10.5 EO/PO	70.0
Nonionic used in series 3	
Neodol 25-7	70.0
Tallow alcohol + 9 EO	68.5
Tallow alcohol + 11 EO	73.0
Tallow alcohol + 14 EO	71.0
Anionic-Nonionic used in series 4	
NaLAS Neodol 25-7	68.0
NaLAS Tallow alcohol + 11 EO	73.0
NaTES Tallow alcohol + 11 EO	73.0

TABLE X

Formulation of 50% Active Detergents

Component	Weight, %
Nonionic	37.5
NaLAS	12.5
Triethanolamine	5.0
Ethanol	6.0
KCl	1.0
Water	38.0

TABLE XI

Formulation for 30% Detergents without Ethanol

Component	Weight, %
Nonionic	22.5
NaLAS	7.5
Triethanolamine	2.0
Water	68.0

Again the Neodol 25-7 and the 10.5-, 13- and 14-mole ethylene oxide/propylene oxide adducts of tallow alcohol were used as the nonionics. The basic formulation is shown in Table XI. The one based on Neodol 25-7 was clear at 4.4 C but gelled. The system containing the 10.5-mole adduct of tallow alcohol was fluid at 4.4 C but developed a faint haze at 5.0 C whereas the 13.0-mole adduct provided a system that was clear and fluid at 4.4 C. The 14-mole adduct was clear at 4.4 C but gelled at 3.9 C. These data certainly suggest that suitable 30% active formulations can be prepared using little or no ethanol with these ethylene oxide/propylene oxide adducts of tallow alcohol.

Another series was prepared in which no ethanol was used but a small amount of sodium xylene sulfonate was incorporated as a hydrotrope. Two nonionics were used, the Neodol 25-7 and the 10.5-mole ethylene oxide/propylene oxide adduct of tallow alcohol (Table XII). The system which contained the Neodol 25-7 became hazy at 18 C and gelled at 4.4 C. That which contained the 10.5 mole ethylene oxide/propylene oxide adduct of tallow alcohol was clear and fluid at 4.4 C.

TABLE XII

Basic Formulation for 30% Detergent Using Sodium Xylene Sulfonate

Component	Weight, %
Nonionic	22.5
NaLAS	7.5
Triethanolamine	2.0
NaXS	0.8
Water	67.2

SULFATION OF TALLOW ALCOHOL

An attempt was made to sulfate tallow alcohol in the Sherex laboratories. Since we are not equipped for continuous sulfation, batch sulfation was tried, using chlorosulfonic acid. Equivalent quantities of alcohol and chlorosulfonic acid were used. The sulfation temperature was 50-55 C with continuous agitation. The reaction mass was swept with dry nitrogen during the sulfation to remove byproduct HCl. The reaction time was ca. 30 min. Nitrogen sweeping was continued for 10 min after all of the chlorosulfonic acid was added. The intermediate sulfuric acid ester was then neutralized with a slight excess of 10% aqueous sodium hydroxide. The aqueous media was kept on the alkaline side throughout the neutralization. A ca. 25% active system resulted after neutralization and final pH adjustment to 7.5.

The resulting product was a heavy paste at room temperature with a Gardner color between 5 and 6. Eighty-three to 85% of the alcohol was converted and less than 50% of the double bonds remained in the finished product. Double bond attack obviously took place, but no further identification of the resulting product was done since batch sulfation of tallow alcohol in this manner does not appear suitable or promising. The product did have decent surface activity showing a surface tension of 30.9 dyne/cm and an interfacial tension of 7.0 dyne/cm at the 0.025% active level at 23 C. By the Ross-Miles foam test the product gave 155 mm foam height in deionized water at 25 C but only 11 mm in 150 ppm hard water. The data indicate that tallow alcohol should be sulfated continuously and that in all likelihood sulfur trioxide should be the sulfating agent.

A LOOK AHEAD

It is expected that during the next decade the use of C_{16-18} fatty alcohols derived from triglycerides, particularly those containing 40-50% oleyl alcohol such as tallow alcohol, are going to become increasingly important, especially in the US market. This increase will come about because of an abundant raw material supply and because of more stable and lower feedstock prices and much lower energy requirements for the production of these alcohols than those for synthetic saturated fatty alcohols from petroleum and natural gas feedstocks. Coconut fatty alcohols from triglycerides will also remain important but will tend to have fluctuating and higher prices than those from tallow.

Proper design of nonionic detergent molecules and proper formulation in heavy-duty liquid detergent systems will significantly spur the use of these C_{16-18} fatty alcohols, both saturated and unsaturated, with the greatest increases coming in the use of such alcohols with an IV of 45-55.

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