Fatty Acid Derivatives: Important Surfactants for Household, Cosmetic and Industrial Purposes

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ABSTRACT

This paper reviews selected surfactants obtained from fatty acids. Because of their indispensible properties, some of these surfactants have already been in use for a long time, whereas others, such as sucrose esters or ester sulfonates, are only beginning to be used. However, all these surfactants have in common the fact that they are highly acceptable to the environment, characterized by their skin tolerance, good biological degradability and low toxicity. With consumer awareness becoming more and more apparent, these are noteworthy properties from which we can expect that surfactants prepared from fats will increase in importance in the future.

INTRODUCTION

Since the dramatic rise in oil prices, surfactants based on natural fats and oils and fatty acids obtained therefrom have gained in importance. Important raw materials in the detergents industry, such as fatty alcohols and the derivatives prepared from these compounds—such as ethoxylates, sulfates and ether sulfates—are today manufactured ever more frequently and in significant amounts from fatty acids or fatty acid methyl esters, as well as from petrochemical raw materials. Furthermore, a large number of fatty acid derivatives which cannot be obtained at all from petrochemical parent substances are used as surfactant raw materials in conversion industries.

Figure 1 shows an overview of the fatty acid derivatives discussed in this paper, as well as a schematic classification into the fields of application.

Neutralization, esterification, amidation, ethoxylation or condensation of the fatty acids obtained by splitting fats and oils gives the corresponding surfactants or emulsifiers, such as soaps, mono- and diglycerides, sugar esters, alkanolamides, polyglycol esters and imidazolines.

Fatty amines obtained via the fatty acid nitrile stage can lead to fatty amine ethoxylates and amine oxides by ethoxylation or oxidation. The quaternary salts which can also be obtained from the fatty amines are discussed elsewhere.

The essential fields of application of these fatty acid derivatives are cosmetics, detergent powders, detergent liquids, fabric softeners, corrosion inhibitors, textile auxiliaries and foodstuffs. Fatty amines and their derivatives likewise have a wide spectrum of uses.

Finally, the ester sulfonates obtainable by sulfonation of fatty acid methyl esters with sulfur trioxide should be mentioned.

Reactions with Amines

A number of these products are obtained by reacting fatty acids with amines. The most important amines are shown in Scheme 1.

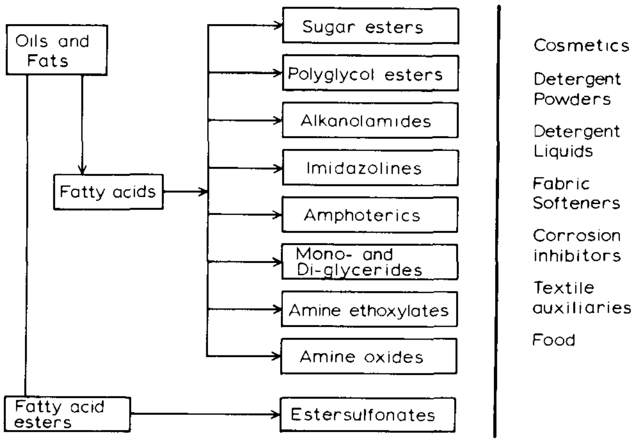
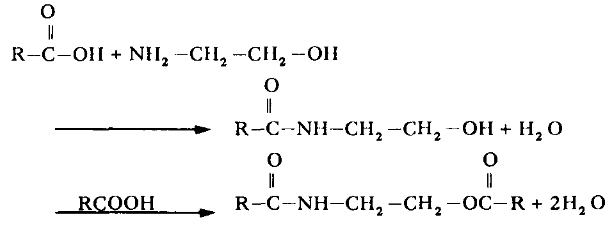


FIG. 1. Fatty acid derivatives.

$H_2NCH_2-CH_2-OH$	Monoethanolamine
$HN\genfrac{}{}{0pt}{}{\diagup CH_2-CH_2-OH}{\diagdown CH_2-CH_2-OH}$	Diethanolamine
$H_2N-CH_2-CH_2-NH-CH_2-CH_2-NH_2$	Diethylenetriamine
$H_2N-CH_2-CH_2-NH-CH_2-CH_2-OH$	Hydroethylethylenediamine

SCHEME 1



$$R-\overset{O}{\overset{\|}{C}}-OH + NH_2-CH_2-CH_2-OH \longrightarrow R-\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_2-OH + H_2O$$

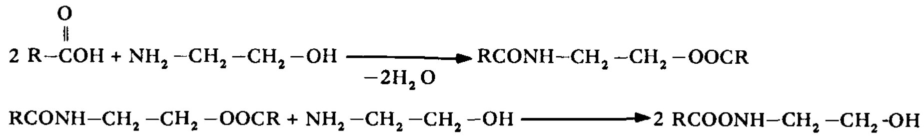
$$\xrightarrow{RCOOH} R-\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_2-O\overset{O}{\overset{\|}{C}}-R + 2H_2O$$

SCHEME 2

Monoethanolamine and diethanolamine, which are prepared by reacting ammonia with ethylene oxide, are reacted with fatty acids at temperatures above 100 C, usually at 180 C. In the case of monoethanolamine, water is eliminated and the desired amide is formed, together with the fatty acid monoethanolamide ester byproduct, as shown in Scheme 2.

The amide content at a reaction temperature of 180 C is on average 94-95% (1). Over 99% of the desired fatty acid monoethanolamide is obtained if 2 moles of fatty acid and 1 mole of monoethanolamine are first reacted to give the fatty acid acylaminoethyl ester, which is then transesterified with a further mole of monoethanolamine (2) (see Scheme 3.

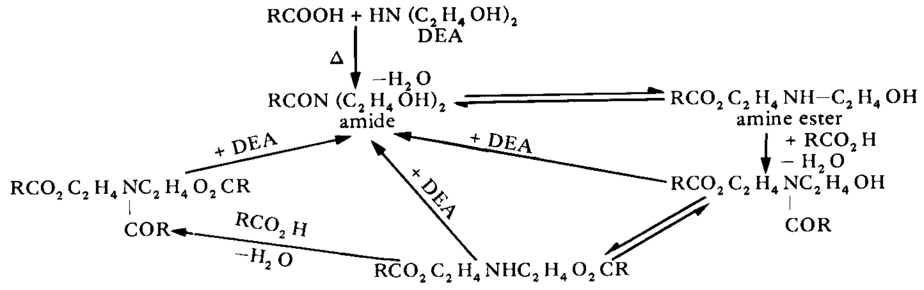
The reaction of diethanolamine with fatty acid is substantially more complicated. Besides the amide, the amine ester is formed, which reacts with an excess of diethanolamine, directly or via other intermediates, to give the desired diethanolamide (3) (Scheme 4). The excess of diethanolamine in the reaction product automatically results in the amine salt of the fatty acid, besides the free amine.



$$2\ R-\overset{O}{\overset{\|}{C}}OH + NH_2-CH_2-CH_2-OH \xrightarrow[-2H_2O]{} RCONH-CH_2-CH_2-OOCR$$

$$RCONH-CH_2-CH_2-OOCR + NH_2-CH_2-CH_2-OH \longrightarrow 2\ RCOONH-CH_2-CH_2\text{-}OH$$

SCHEME 3



SCHEME 4

TABLE I

Typical Composition of Diethanolamides (4)

Components	2:1 amide from the fatty acid (% weight)	1:1 amide from the methyl ester (% weight)
Diethanolamide	65	90
Free DEA	22	5
Amine salt	10	trace
Amide ester	1	4
Water	2	trace
Methanol	–	0.2
Methyl ester	–	0.8

The reaction proceeds more uniformly if the methyl ester is used instead of the free fatty acid. The reaction, which is catalyzed by bases, gives a diethanolamide content of ca. 90% at a lower temperature.

Table I compares the composition of the reaction products from the free acid and the methyl ester.

Because of their high purity, the so-called superamides prepared from the methyl ester and also the monoethanolamides are used for the preparation of shampoos. In this application, their effectiveness is based on foam stabilization and viscosity improvement. The foam stabilization becomes effective where there is a large amount of grease (5). In the case of fatty alcohol ether sulfate formulations and fatty alcohol sulfate formulations, the foaming ability is greatly reduced if a large amount of grease is present. The addition of 10% fatty acid monoethanolamides based on the surfactant concentration retains the foaming ability almost at a constant level, even as the amount of grease increases. The influence of alkylolamides on viscosity results from a viscosity reserve which becomes effective when ether sulfate solution formulations are diluted (6).

The skin tolerance of surfactant formulations can also be improved by adding fatty acid alkylolamides (7). The addition of fatty acid alkylolamides reduces the zein number, which is equivalent to a better skin tolerance.

The very good rust prevention properties of fatty acid alkylolamides are also to be emphasized. Although they are themselves poor emulsifiers, they improve the stability of anionic and nonionic emulsions and the lubricating power of the emulsified oil. They are therefore used, in amounts of 1-5%, in cooling lubricants, such as drilling oils and cutting oils, and are almost always essential constituents of anticorrosion additive formulations. Oil-soluble, liquid types, e.g., oleic acid diethanolamide, are usually employed.

More hydrophilic types, e.g., coconut oil acid diethanolamide, which still contains free amine and amine salts, is used preferably for aqueous grinding fluids (e.g., vibratory abrasives). Because of their good anticorrosion and dispersing properties, which also manifest themselves in a good soil-suspending power, they improve surface gloss, especially on colored metals and aluminum.

Fatty acid alkylolamides—usually diethanolamides of stearic acid—are used as textile-greasing agents, sometimes in combination with fatty acid polyglycol esters with blocked end groups. When added on to the usual mineral oil-based greases, they substantially improve the mode of action of combing greases.

Useful raw materials for cosmetics are obtained by reacting fatty acid monoalkanolamides with maleic acid and then reacting the product with sodium sulfite to give the sulfosuccinic acid monoester. Because of their high foaming power and their foam stability, these products are also used in carpet shampoos, in combination with fatty alcohol sulfates or olefin sulfonates (8,9).

Finally, fatty acid amides obtained by reacting the fatty acid with certain long-chain amines form the basis for the pearlescent effect frequently desired in shampoos.

The fact that the fatty acid diethanolamides can also be prepared directly from fats and oils should not be overlooked (see Scheme 5). The glycerol obtained in the reaction, which is run at ca. 180 C, remains in the product and is of no trouble in the abovementioned fields of application.

A diethanolamide prepared from coconut oil contains ca. 80% of the desired amide, 9% of glycerol and, as secondary constituents, also 7% of salts of the fatty acid and 2% of free diethanolamine.

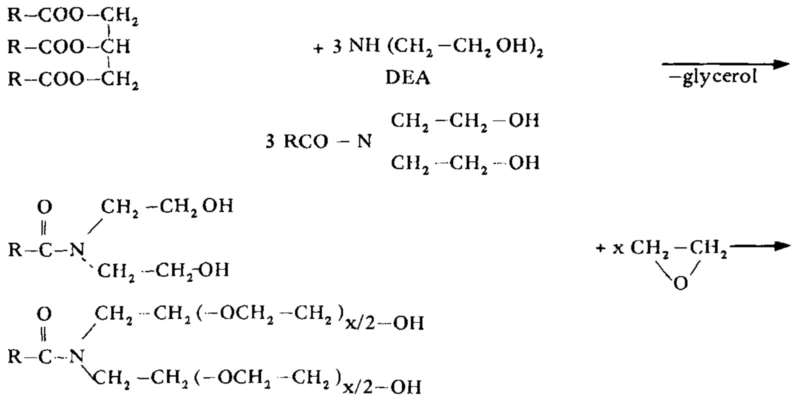
The reaction of alkylolamides with ethylene oxide gives products which have a similar pattern of properties but a higher water-solubility and therefore are frequently preferable to the amides, depending on the field of application. The reaction in Scheme 5 has been simplified.

In reality, an equilibrium is established between the alkanolamide, the alkanolamine ester, the fatty acid acylaminoalkyl ester and the alkanolamine in the ethoxylation of fatty acid alkanolamides, this equilibrium being to a greater or lesser extent on the side of the amide, depending on the nature of the fatty acid. An ethoxylate mixture of amide ethoxylate, amine ethoxylate, ester amine ethoxylate and fatty acid ethoxylate is obtained in all cases (10).

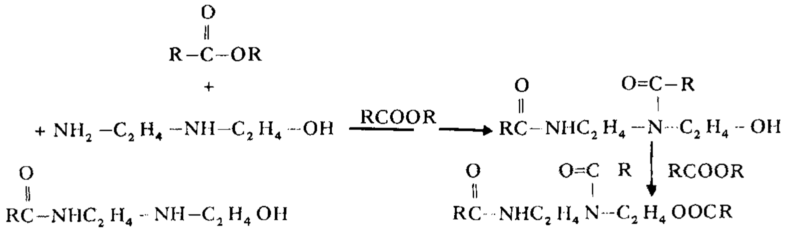
The following compounds are obtained as the main reaction products when fatty acids or the methyl esters are reacted with β-hydroxyethylethylenediamine at low temperatures (Scheme 6). These mono-, di- and triacylamines have textile-softening properties (11) and are recommended for use in rinsing bath finishes (12) and in light-duty detergents (13). They are most effective in light-duty detergents at an acyl/amine ratio of 0.9:1 (14).

At higher temperatures, 2-alkylimidazolines are formed, via the amide stage, in the reaction of fatty acids and β-hydroxyethylethylenediamine (see Scheme 7).

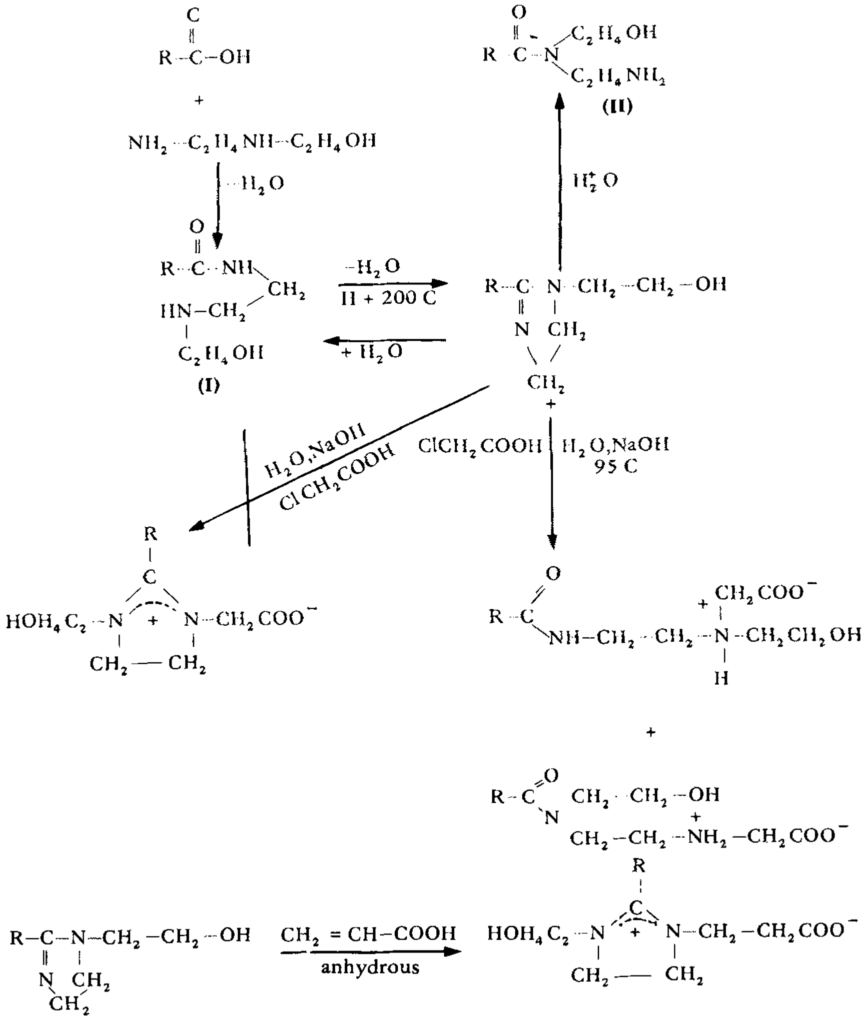
In the condensation reaction, the amide (**I**) is first formed and is then cyclized to the 2-alkylimidazoline at temperatures of ca. 200 C under acid catalysis. As described in several recent publications, 2-alkylimidazolines are very sensitive to hydrolysis and decyclize particularly rapidly to the amides **I** and **II** in an alkaline medium merely in the presence of atmospheric moisture.



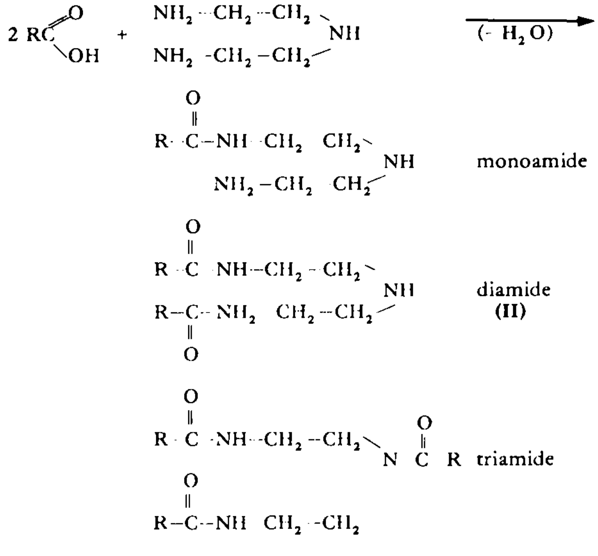
SCHEME 5



SCHEME 6



SCHEME 7



SCHEME 8

It was possible to demonstrate by spectral analysis that the open amphoteric structures derived from the two amides **I** and **II** are therefore formed in the reaction with chloroacetic acid in an alkaline aqueous medium, and not the amphoteric imidazoline derivative (15).

However, the imidazoline ring structure in the amphoteric form is retained if acrylic acid is added onto the starting imidazoline in an anhydrous medium under the action of heat. The resulting reaction products contain between 80 and 100% of the imidazoline ampholyte, depending on the starting compound, the ring structure being retained in the acid medium (16). Significant hydrolysis of the ring takes place only at pH values above 9, and this also leads to the open-chain amide structures.

Because of their ampholytic character, compounds having the structures just described are usually particularly compatible with other types of surfactants. They combine a high foaming intensity with good tolerance by the mucous membrane and are therefore suitable for use in high-quality shampoos. Mixtures with more conventional surfactants, such as ether sulfates, are usual, the ampholyte having good foaming properties similar to those of a fatty alcohol ether sulfate (Chemische Werke Hüls AG, unpublished). Investigations have shown that if the liquor contains a large amount of grease, a better foam stability is achieved if the fatty alcohol ether sulfate is combined with the above ampholyte (Chemische Werke Hüls AG, unpublished).

The skin tolerance of fatty alcohol ether sulfates is also substantially improved by adding the same type of ampholyte—as confirmed by the zein test or the saccharase test (17).

As a result of their zwitterion structure, the ampholytes react like cationic surfactants in an acid medium and like anionic surfactants in an alkaline medium. This also explains their stability at low and high pH values. Since, moreover, they are also particularly stable to electrolytes—especially in the case of the salt-free imidazolinium compounds—they can assist in the formulation of highly acid or alkaline liquid cleaning agents, which are preferably used in the industrial sector, e.g., in the cleaning of metals or automobiles. Because of the extreme conditions, such formulations cannot be prepared on the basis of conventional surfactants since these are salted out or unstable under precisely these conditions.

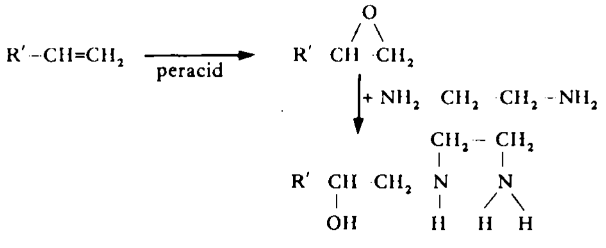
The reaction of fatty acids with polyamines of the diethylenetriamine type at low reaction temperatures gives primarily mono-, di- and triamides (see Scheme 8). These amides can be further reacted, e.g., with ethylene oxide, or are used as such. The reaction product of stearic acid, pelargonic acid and triethylenepentamine is used, for example, as a lubricant in the manufacture of glass fibers or as an emulsifier in plastics dispersions.

At higher temperatures, cyclization to the imidazoline ring also takes place and the diamide **II** preferentially formed reacts, with elimination of more water (Scheme 9). The ring is formed in a yield of up to 95%, depending on the reaction procedure (18). As a rule, the resulting imidazoline is reacted with dimethyl sulfate to give the quaternary imidazolinium methosulfate. These compounds have textile-softening properties, which have a maximum effect if both alkyl radicals contain 16-18 carbon atoms (19). As is known, they are used for fabric softeners, where, in Europe, they have been recently used to an increasing extent in highly concentrated formulations. Since they tend to gel less, they are preferred to distearyldimethylammonium chlorides usually used.

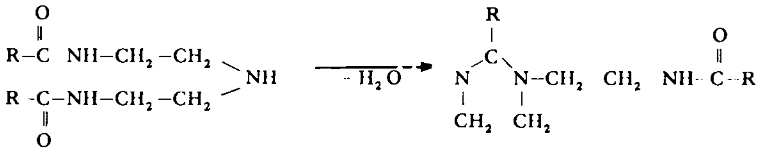
Apart from the above reactions leading to conventional surfactants, the reaction of fatty acids with aliphatic amines provides a wealth of other possibilities. For example, novel imidazoline compounds are obtained if fatty acids are reacted with N-(vic-hydroxyalkyl)-ethylenediamines (20). The latter are accessible by reacting long-chain epoxides with ethylenediamine, the epoxides being obtained from olefins with double bonds in the α-position or in inner positions by oxidation with hydrogen peroxide, via peracids (Scheme 10).

The profile of properties of the quaternary imidazolinium compounds obtained by condensation with fatty acids and with dimethyl sulfate or methyl chloride extends over a broad spectrum, depending on the chain length of the olefin and of the fatty acid used, possible properties of the compounds ranging from bactericidal properties to substantive properties.

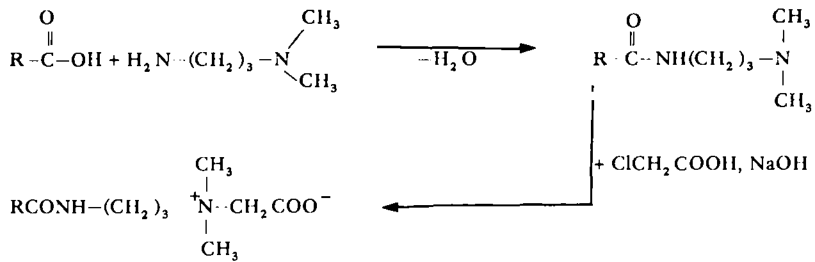
N,N-Dimethylpropanediamine reacts with fatty acids to form the amide, which can be reacted with chloroacetic acid under alkaline conditions to give the fatty amide-alkylbetaine (Scheme 11). The resulting betaines are chiefly distinguished by their good skin tolerance. In comparison with linear alkylbenzene sulfonates (LABS), sodium lauryl sulfate and sodium lauryl ether sulfate, again tested by the



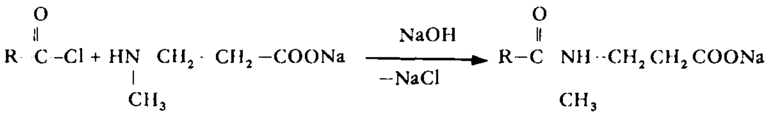
SCHEME 10



SCHEME 9



SCHEME 11



SCHEME 12

zein test, the betaine can be classified as a reagent which is gentle to the skin (21).

The products have good foaming power and influence the viscosity properties of other surfactants. A particular property is that their foaming power is virtually retained in the presence of soap (21). These betaines provide the possibility of preparing high-quality shampoos or liquid soaps, in which they are usually formulated as a mixture with other surfactants, such as ether sulfates.

Betaines have considerable fungicidal action, especially against Staphylococci and Corynebacteria. Since these are held chiefly responsible for the evolution of odor, betaines of the type described also have a deodorizing action (22).

Since linear compounds have better lubricating properties in textile preparation, fatty acid alkylolamides are frequently not used, since they can form piperazine compounds by cyclization during preparation. Other amines, e.g., γ-aminopropyl glycol ether, which can be prepared from ethyleneglycol and acrylonitrile with subsequent hydrogenation, are used instead. The amide obtained from this amine and fatty acid retains its linear structure even under ethoxylation conditions.

Finally, fatty acid chlorides react with sarcosinate in an aqueous alkaline medium to form the fatty acid sarcoside (Scheme 12). In the case of oleic acid, products which have a particular lubricating action in polyester fiber preparations are obtained.

Fatty acid-protein condensates obtained by reacting fatty acid chlorides with protein hydrolysates are advantageously used for boiling out grey cotton wool because of their good stability to electrolytes and hard water, especially in the alkaline range, associated with a high levelling and dispersing action.

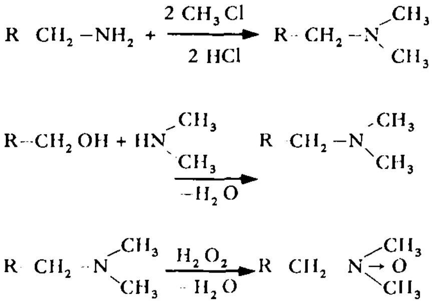
Primary, secondary, tertiary and quaternary fatty amines can be made from fatty acids via the nitrile stage. These fatty amines, on a large industrial scale, are already valuable raw materials as such.

Primary fatty amines can be converted into the fatty amine ethoxylates by ethoxylation, i.e., by reaction with ethylene oxide, and these products can be used as surfactants, especially in an alkaline medium.

Amine Oxides

An interesting product class of amine oxides can be prepared from tertiary amines, which are obtained either from primary fatty amines by dialkylation or from fatty alcohols by reaction with dialkylamines.

Subsequent reaction with a molar excess of 35% strength hydrogen peroxide in an aqueous medium at temperatures between 60 and 70 C gives the corresponding amine oxide in almost quantitative yield. The reaction can be accelerated by the presence of formates (23) (see Scheme 13).



SCHEME 13

The amine oxides, which behave like nonionic surfactants in neutral and alkaline media, are considerably superior to lauryl sulfate in the region of the critical micelle concentration. However, their characteristic property is their extremely high foaming power, which is clearly superior to that of lauryl sufate. In comparison with lauryl sulfate, their washing and dispersing powers are also more pronounced in the case of cellulose fibers in the alkaline range and wool in all pH ranges. As well as the foam-improving properties, an antistatic activity results in a substantial improvement in styling capability when hair shampoos containing amine oxide are used (24).

Reactions with Ethylene Oxide

One of the longest-known reactions in which surfactant substances are obtained from fatty acid is the base-catalyzed reaction between fatty acids and ethylene oxide (25). Sodium hydroxide solution, sodium methylate or sodium acetate is as a rule used as the catalyst.

Mixtures of fatty acid polyglycol monoesters and fatty acid polyglycol diesters and polyethylene glycol are always formed on direct ethoxylation. In a first slow stage, addition of up to 1.1 moles of ethylene oxide onto the fatty acid takes place, the monoglycol ester being formed. In a more rapid stage, further ethylene oxide is taken up and the polyglycol ester is formed, a transesterification reaction giving the fatty acid polyglycol diester and polyethylene glycol simultaneously taking place (26-29) (see Scheme 14). In adding 7 moles of ethylene oxide onto oleic acid, e.g., an MOE/DIE/PEG ratio of 2:1:1 is obtained after addition of several moles of ethylene oxide, which means a polyethylene glycol content of ca. 15-20% by weight (30).

Fatty acid polyglycol esters are good oil-in-water emulsifiers, depending on the degree of ethoxylation. Needless to say, the emulsifying ability decreases rapidly as the polyethylene glycol content increases, i.e., the products obtained by conventional processes lead to unstable emulsions.

$$RCOOH + C_2H_4O \rightarrow RCOOC_2H_4OH$$

$$RCOOC_2H_4OH + (n\text{-}1)\,C_2H_4O \rightarrow RCOO(C_2H_4O)_nH$$

$$2\,RCOO(C_2H_4O)_nH \rightleftharpoons RCOO(C_2H_4O)_nOCR + HO(C_2H_4O)_nH$$

SCHEME 14

A possibility of drastically reducing the polyethylene glycol content is based on the observation that water resulting from the condensation of the fatty acid monoglycol ester and free fatty acid already forms in the first stage of the reaction, free ethylene glycol also being present (31).

If the reaction is therefore interrupted after the addition of 0.25 to ca. 1 mole of ethylene oxide—i.e., during the start-up phase—and the resulting water of reaction/glycol mixture is evaporated off, products with low polyethylene glycol contents are obtained when the reaction is continued; the higher diester content which is, of course, formed in the reaction is of no trouble in the preparation of stable emulsions.

Figure 2 shows the percentage composition of the reaction mixture of oleic acid with the addition of 7 moles of ethylene oxide. The molar addition of ethylene oxide at which the reaction has been interrupted is shown on the abscissa. In comparison, the points show the composition from the reaction carried out under normal conditions, leading to significantly higher PEG contents.

There has been no lack of attempts also to reduce the diester content. This is achieved in the reaction of 1 mole of fatty acid with 1 mole of ethylene oxide if fatty amines or amine oxides are used as catalysts. Fatty acid ethylene glycol monoesters are formed in a yield of between 90 and 100% at a reaction temperature of 70-90 C. Temperatures above 100 C, a higher basicity of catalyst, and an excess of ethylene oxide promote formation of the diester (32).

Conversion of these monoesters to the ester sulfates provides an interesting possibility (Scheme 15). This reaction, which leads directly to anionic surfactants bypassing the hydrogenation stage to give fatty alcohols, is referred to, but the products are not described in more detail (32).

Fatty acid polyglycol esters are generally less water-soluble than fatty alcohol ethoxylates. Products with a low degree of ethoxylation are used chiefly as emulsifiers, since they have a good oil-solubility. The main uses of these products are in the textile industry and in cosmetics. In the textile sector, they are chiefly used as emulsifiers in fiber greasing, where they ensure better distribution of the mineral or vegetable oils used for greasing (33). In the finishing industry, they prevent electrostatic charging of the fibers, which is based on the uptake of water from the air. At relative atmospheric humidities of 60-80%, a maximum effect is found with an ethylene oxide content of 10-15 moles per mole of fatty acid (34).

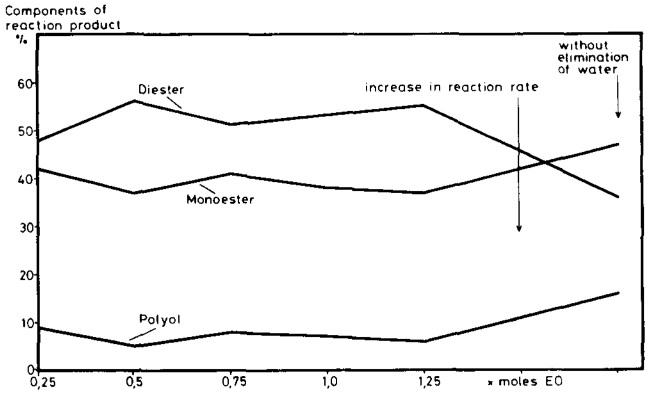
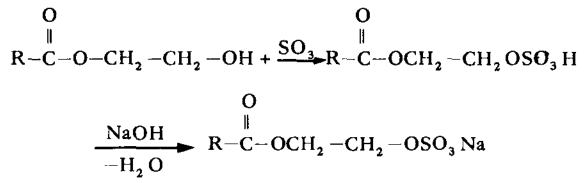


FIG. 2. Oleic acid + 7 EO: elimination of water/glycol after addition of x moles EO (31).



$$R\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}CH_2\text{-}CH_2\text{-}OH + \xrightarrow{SO_3} R\text{-}\overset{\overset{O}{\|}}{C}\text{-}OCH_2\text{-}CH_2OSO_3H$$

$$\xrightarrow[-H_2O]{NaOH} R\text{-}\overset{\overset{O}{\|}}{C}\text{-}OCH_2\text{-}CH_2\text{-}OSO_3Na$$

SCHEME 15

In cosmetics, the mild skin reaction of these products is most important and the good emulsifying action is used for the most diverse purposes. Thus, for example, polyethylene glycol (PEG)-600-laurate dissolves pyrenones in water, PEG-400-laurate gives clear solutions with DDT which can easily be emulsified with water PEG-1,000-laurate emulsifies perfume oils and essences, and, finally, PEG-1,500-stearate is used as an emulsifier for creams (35).

Fatty acid polyglycol esters have also recently been used for combatting oil pollution, where, besides their emulsifying and dispersing properties, their relatively low toxicity towards marine fauna plays a particular role (36,37).

Fatty Acid Esters

Fatty acid esters include fatty acid monoglycerides and diglycerides which are obtained by glycerinolysis of triglycerides. This reaction is run with an excess of glycerol at temperatures of 200-250 C (38). The reaction is generally done under an inert gas atmosphere, especially if unsaturated fats are used.

After a reaction time of 30-60 min, the reaction mixture as a rule contains 35-60% of monoglycerides and 35-50% of diglycerides, in addition to triglyceride, glycerol and fatty acids. These mixtures of monoglyceride and diglyceride are used as emulsifiers in the foodstuffs industry and in cosmetics (39,40). Reaction products, e.g., succinylated monoglycerides or ethoxylated monoglycerides and diglycerides, also are frequently used for these purposes.

The emulsifying action of the monoglycerides is superior to that of the diglycerides. These are obtained by molecular distillation of the monoglyceride/diglyceride mixtures (40).

Sugar esters of fatty acids have been investigated extensively during the last 20 years; they deserve particular consideration since they can be prepared from renewable resources and are physiologically, dermatologically and biologically acceptable surfactants (41).

Sucrose Esters

Besides the fatty acid esters of sorbitol and its dehydration products, which are used, especially in the USA, as water-in-oil emulsifiers in the foodstuffs industry or in ethoxylated form as oil-in-water emulsifiers, the fatty acid esters of sucrose have chiefly been investigated in which the primary hydroxyl groups are preferentially replaced during the transesterification process between the fatty acid methyl ester and the sucrose.

Pioneering work in the preparation of this class of surfactants has been done by Foster D. Snell Inc., New York, which has utilized the polar properties of DMF and DMSO, which permit a transesterification reaction in a homogeneous medium. The reaction is run under anhydrous conditions and is catalyzed by potassium carbonate at ca. 90 C.

The cumbersome working up of the solvents has led to a further development of the process. In the so-called Nebraska-Snell process (42), propylene glycol, which distills off during the reaction, is used as a solvent for the sucrose, while the methyl ester, which is insoluble therein, is made available to the reactant in the form of a microemulsion. By weight, 85% of sucrose monoester and 15% by weight of sucrose diester are formed at a molar ratio of sucrose to methyl ester of 1.5:1. In this case also a relatively simple extraction stage must be run for purification of the reaction product.

The sucrose monoesters show surfactant properties. Besides their water-solubility, which decreases as the chain length of the fatty acid increases, they correspond in respect of the surface tension of their aqueous solutions and of their washing power, tested in formulations, to the alkylbenzene sulfonates, although they differ significantly in foaming power and in wetting action (43). The sucrose monoesters tend to foam less and have a lower wetting power; they are particularly suitable as emulsifiers—frequently in combination with other emulsifiers—for the preparation of stable oil-in-water emulsions. Conversely, because of their higher lipophilicity, the sucrose diesters are water-in-oil emulsifiers. These properties, together with their physiological acceptability, predestine the sucrose esters for use in cosmetics and the foodstuffs industry.

To avoid expensive working up of the solvents and also losses in solvents, triglycerides can also be used directly as the starting materials. In this process, which has become known as the TAL process (44), beef tallow is transesterified with sucrose in the presence of potassium carbonate, without a solvent. A 40% molar excess of sucrose and a relatively large amount of catalyst at a reaction temperature of ca. 125 C results in a product shown in Table II.

On first sight, this reaction product should be suitable for building up emulsions—especially for oil-in-water emulsions—since it contains both hydrophilic and hydrophobic components. The hydrophile-lipophile balance (HLB) value could also be changed by the reaction procedure.

Besides this complex product mixture (I)*, two other products which, after extraction with solvents, consisted on the one hand of a mixture of sucrose esters and potassium soaps (II)* and on the other hand of the pure sucrose esters (III)*, have been used for washing experiments. (*Products of Tate & Lyle Ltd., Reading, United Kingdom.)

Figure 3 shows the results of the individual washing power of these products by themselves and in combination with sodium tripolyphosphate (STPP), in comparison with LABS. On both test-soiled fabrics, product I—i.e., the original reaction mixture—exhibits a poor washing power in comparison with the other products, i.e., even in comparison with LABS, whereas the two purified products II and III give impressive results both at 90 C on cotton and at 60 C on polyester mixed fabric. In the case of the 60 C wash, even better results are achieved in the presence of STPP than with LABS. This should be attributable to the nonionic character of the products.

One formulation (Fig. 4), containing no surfactants other than products II and III and only containing the builder system described, gave almost comparable values to those of a commercial product (H) in a washing machine test using ballast fabric and cotton test fabric at 95 C with 5 g/L of detergent, and only product III, which is built up on the basis of the pure sucrose ester, gave comparable results at 60 C.

The foaming properties of the formulations investigated were evaluated as being equivalent in a rotary-type machine.

Since no redeposition tests have been made and the products have also not been subjected to the conditions of the hot-air spray-drying process—it is questionable whether the ester bond withstands these conditions—it is of course not possible to comment generally on the use of sucrose esters in the detergents field.

TABLE II

Composition of a Reaction Product Obtained by the TAL Process

Components	% by weight
Sucrose monoester	27
Sucrose diester	3
Sucrose	13
Triglycerides	3
Diglycerides	9
Monoglycerides	15
Potassium soaps	30

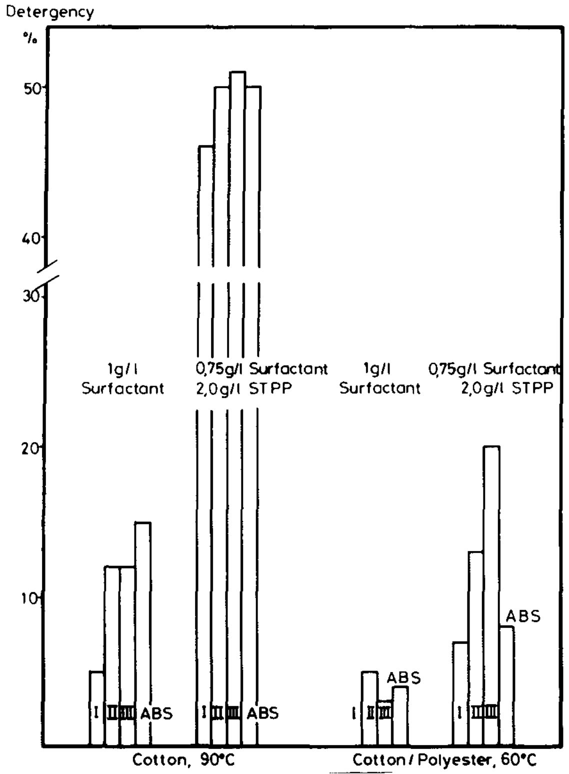


FIG. 3. Detergency of sucrose esters compared to linear alkylbenzene sulfonate (LABS) at 13° German hardness.

Ester Sulfonates

A reaction should be discussed which is fascinating for its simplicity, since anionic surfactants are obtained directly, i.e., without intermediates, from fatty acid esters—as a rule from the methyl esters. The process in question is the reaction of fatty acid esters with gaseous sulfur trioxide with formation of ester sulfonates (45,46) (Scheme 16).

If this reaction, which as a rule takes place in a falling film reactor, is run with tallow fatty acid esters, these ester sulfonates are distinguished by a good textile-washing power, which is retained even if the water is relatively hard (45). The disadvantage of this compound is its poor water-solubility, leading to pasty formulations at concentrations as low as ca. 30%. In our own investigations, we have ascertained the properties of the ester sulfonate obtained from coconut oil acid methyl ester. Besides the fundamental properties, such as surface tension, critical micelle concentration, etc., we have directed our attention to the possible use of this compound in shampoos, since the ester sulfonates have a comparable skin tolerance to the ether sulfates (47).

For this intended application, the important properties are solubility, foaming power and good viscosity of the surfactant to be used.

Figure 5 shows the solubility properties—demonstrated by the clear point—of a coconut oil acid ester sulfonate (CES) as a function of the concentration and in comparison

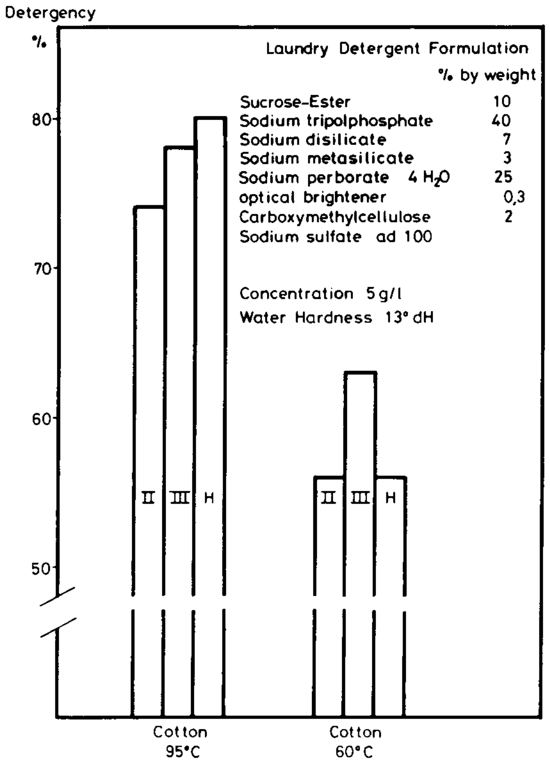


FIG. 4. Detergency of formulations based on fatty acid esters of sucrose compared to laundry detergent H.

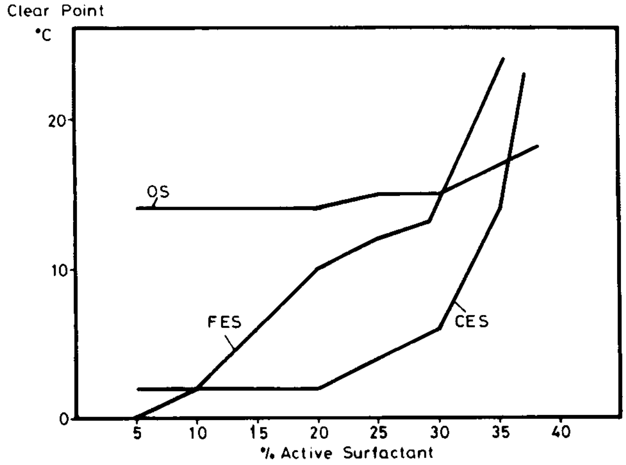
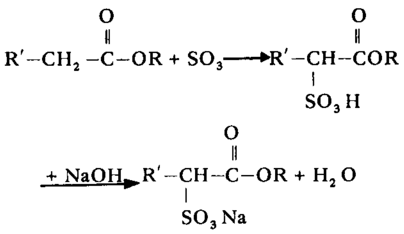


FIG. 5. Solubility of sodium coco fatty methyl ester sulfonate (CES), sodium C_{14-16}-olefin sulfonate (OS) and sodium C_{12-14}-fatty alcohol ether sulfate (FES).

with a C_{14}-C_{16} olefin sulfonate (OS) and a C_{12}-C_{14} fatty alcohol ether sulfate (FES). The ester sulfonate shows clearly more favorable properties over the entire concentration range. Clear points of 0 C are obtained over a wide concentration range (10-20% by weight).

The foaming power of the ester sulfonate—although shown without a large grease content here (Fig. 6)—is comparable with that of the other two types of surfactant, although the stability of the foam is slightly poorer.

The influence of the ester sulfonates on viscosity proves to be a difficult problem. Their property of highly diluting other surfactant solutions is known (45). This also manifests itself (Fig. 7) in the mixtures with ether sulfates, in which the ether sulfonates reduce the starting viscosity of a 10% strength ether sulfate solution of ca. 4,000 mPa.sec to viscosity values below 10 mPa.sec, very low viscosities being obtained with a mixing ratio of ether sulfate/ester



$$R'-CH_2-\overset{O}{\overset{\|}{C}}-OR + SO_3 \longrightarrow R'-\underset{SO_3H}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}OR$$

$$\xrightarrow{+\,NaOH} R'-\underset{SO_3Na}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-OR + H_2O$$

SCHEME 16

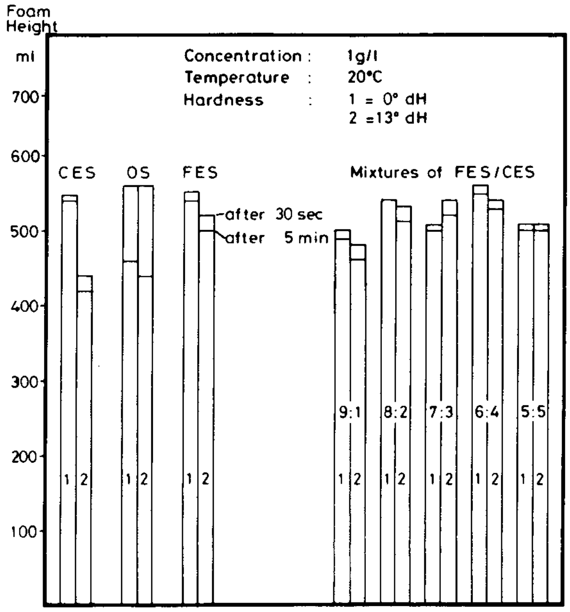


FIG. 6. Foam height of coco fatty acid methyl ester sulfonate (CES), C_{14-16}-olefin sulfonate (OS) and C_{12-14}-fatty alcohol ether sulfate (FES) (all sodium salts).

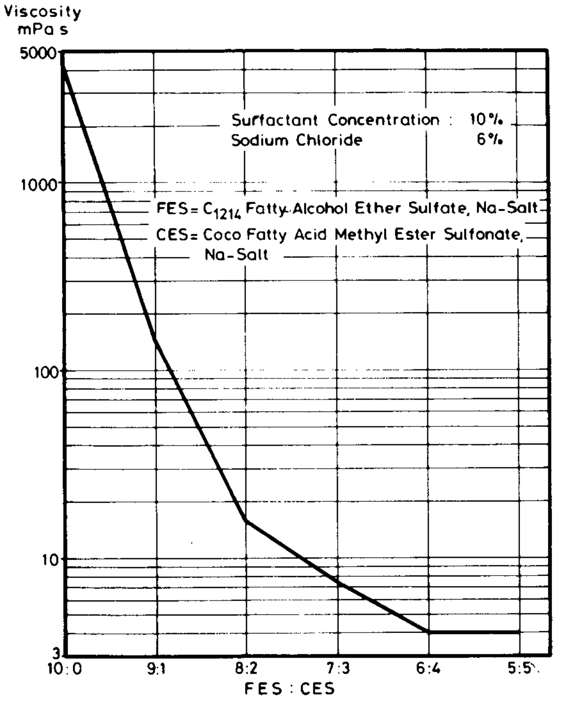


FIG. 7. Viscosity of mixtures FES/CES in presence of 6% sodium chloride.

sulfonate of as low as 9:1. With fatty amide alkylbetaines also, higher viscosity values are obtained only at higher total concentrations (30% by weight) (Fig. 8).

The results shown here are only examples. Further re-

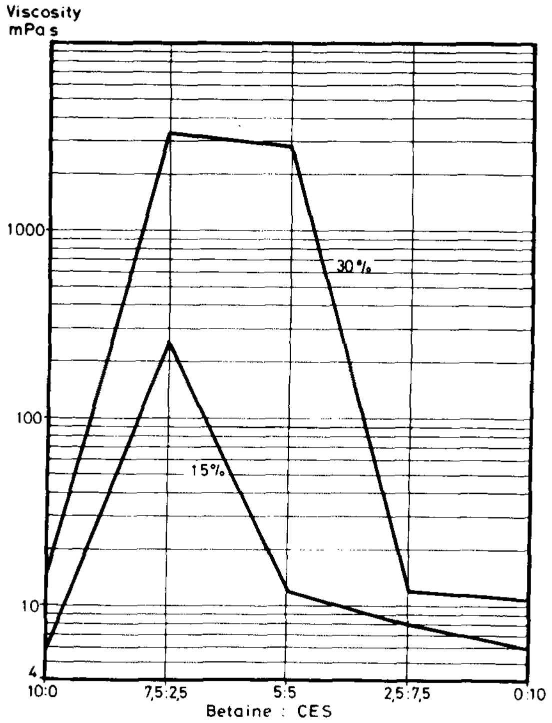


FIG. 8. Variation of viscosity in mixtures of fatty amido alkyl betaine and coco fatty acid methyl ester sulfonate monoethanol amine salt (CES), 15% and 30%.

search is aimed at obtaining marketable formulations with this interesting raw material. Use as a component of carpet shampoos has already been shown to be a possibility for ester sulfonates based on coconut oil acid methyl ester. When mixed with sulfosuccinates, they have the same properties in respect to cleaning action and foaming power as the mixtures of sulfosuccinate and fatty alcohol sulfate or olefin sulfonate known hitherto. However, in respect to the dry residue, they are superior to these known mixtures and thus also more effectively delay resoiling.

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