• Technical

α-Sulfonated Fatty Acids and Esters: Manufacturing Process, Properties, and Applications

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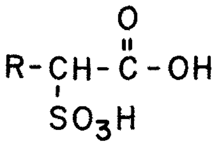
ABSTRACT

α-Sulfonated fatty acid esters, because of their wide-range of application and biological properties, represent an interesting class of surfactants. A technical method for the preparation of α-sulfonated fatty acid esters is described. By using special reaction conditions it is possible to α-sulfonate saturated fatty esters directly without the use of solvents. The use of gaseous SO_3 gives the product in greater than 97% yield. A process for the bleaching of the α-sulfonated fatty esters has been developed, whereby a product of faultless color is produced without the necessity of further purification or separation techniques. The sulfonation and bleaching processes operate continuously. The process has been tried successfully on a commercial scale using the methyl esters of technical fatty acids. Methods for the preparation of α-sulfonated fatty acids are given. The chemical, technical, and biological properties of the α-sulfonated fatty acids and their esters are discussed. α-Sulfonated fatty esters possess good washing and foaming properties, have good biological degradability, possess good skin compatibility and low acute toxicity. They can be considered as surfactant components for phosphate-free or low-phosphate detergents. α-Sulfonated fatty acids and esters also possess other favorable technical properties which allow them to be used in cosmetics, as auxiliary agents in the production of fibers, plastics, and rubber, and in leather manufacture.

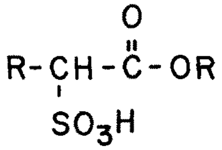
INTRODUCTION

Salts of α-sulfonated fatty acids (abbreviated as fatty acid sulfonates [FAS]) and salts of α-sulfonated fatty esters (abbreviated as ester sulfonates [ES]) have been known for a considerable period of time. Their chemical formulas are:



$$R\text{-}\underset{SO_3H}{CH}\text{-}\overset{\overset{O}{\|}}{C}\text{-}OH$$

α-sulfonated fatty acids



$$R\text{-}\underset{SO_3H}{CH}\text{-}\overset{\overset{O}{\|}}{C}\text{-}OR$$

α-sulfonated fatty acid esters

Because of their superior properties, the ES are of greater practical importance than are FAS. However, because of the lack of a simple, economical manufacturing process, they have received little attention. Therefore, at the end of the 1950's we began to develop a technically practical method for preparing ES of exceptional quality (1). On economic grounds, this could only proceed by direct sulfonation of fatty esters, especially methyl esters. At ca. the same time, Knaggs and co-workers at the Stephan Chemical Company (2) carried out a study concerned with ES which was primarily concerned with the range of application and biological properties of these substances.

The problem concerning the direct sulfonation of fatty esters was that the α-hydrogen atoms, due to the neighboring ester group, were only weakly activated. Therefore, to achieve sulfonation, stronger sulfonating agents and more drastic reaction conditions were required. However, under these conditions the side reactions which normally occurred during sulfonation became more pronounced, leading to the formation of darkly colored decomposition products. Up to the beginning of the 1960's, a technically useful manufacturing process was unknown for ES of an acceptable quality without the necessity of further purification steps. The only method by which it was possible to obtain ES of satisfactory quality was by esterification of pre-formed and purified FAS using the appropriate alcohols (3). However, this method was too troublesome to achieve practical importance.

PROCEDURES

Starting Materials

Esters were derived from unbranched C_8-C_{22} carboxylic acids and from C_1-C_3 alcohols. On economic grounds, the methyl esters of commercial fatty acids were preferred. In particular, we have used the methyl esters (in some cases ethyl esters) from palm kernel oil, coconut oil or tallow. As will be shown later, to produce sulfonated products which can be readily bleached, it was necessary that the original fatty acid esters be hydrogenated to such an extent that their iodine number was less than 0.5. Analytical data for the starting materials are given in Table I. The esters were practically colorless, and SO_3 was used as ca. 5 volume-% mixture with air, dried over Silica gel.

Sulfonation Apparatus

The sulfonation was carried out in various pieces of apparatus in the laboratory, on a pilot plant scale, and on a manufacturing scale. For batch sulfonation in the laboratory, a cylindrical glass vessel of 4 cm inner diameter (ID) and 45 cm ht was used. It was fitted with a cooling jacket, gas inlet tube, gas outlet tube, and an inner thermometer. A gas inlet tube of 8 mm ID led from the top of the apparatus to the bottom of the container. Continuous sulfonation experiments on a laboratory scale were carried out using a thin film reactor. This consisted of a glass tube 1 m long and 6 mm ID fitted with a cooling jacket. The ester was injected into the reactor through a nozzle, thereby forming a film on the inner surface of the glass tube. The ester film reacted with an SO_3:air mixture also introduced at the top of the apparatus. Also connected to this apparatus were a gas separator which served to separate the gaseous and liquid phases, and a heated, extended residence time coil. This apparatus had the function of ensuring that the reaction went to completion. The ester throughput was ca. 600 g/hr, and the SO_3 concentration in the SO_3:air mixture was ca. 5 volume-%.

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[1] Presented at the AOCS Meeting, Mexico City, Mexico, April 1974.

TABLE I

Analytical Data of Starting Materials

Starting material	Acid no.	Iodine no.	Hydroxyl no.	Saponification no.	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}	C_{20}	Average chain length
Hydrogenated palm kernel fatty acid methyl ester	1.2	0.1	2.4	240	1.2	59.1	21.9	8.8	9.0	---	$C_{13.1}$
Hydrogenated tallow fatty acid methyl ester	0.6	0.3	0	196	---	0.7	4.0	29.8	64.6	0.9	$C_{17.6}$

Pilot plant sulfonations were carried out continuously either in a 2 in. Chemithon reactor or a Cascade apparatus with 5 reactors connected together. The 2 in. Chemithon reactor, which is an annular space reactor fitted with a cylindrical rotor (4), had a throughput of ca. 45 kg ester/hr. The standard apparatus was connected to a heated, extended residence time reactor.

The cascade apparatus consisted of 5 cylindrical vessels (each of ca. 7 liter capacity) connected in series. Each was fitted with a cooling jacket, a product and gas inlet tube, a gas outlet tube, and a product outflow tube. The vessels were arranged so that a flow of product from one vessel to the next occurred automatically. An SO_3:air mixture was led into the first four vessels, the fifth vessel serving as an extended residence time reactor. The cascade apparatus had a throughput of ca. 20 kg ester/hr. The sulfonation of fatty acid esters on a production scale was carried out in a 12 in. Chemithon reactor with a throughput of ca. 800 kg ester/hr.

RESULTS AND DISCUSSION

Sulfonation of Fatty Acid Esters

Because of its commercial availability and quality, the most favorable sulfonating agent has been gaseous SO_3 mixed with an inert gas, (preferably 90-95 volume-% air). Figure 1 shows the dependency of the degree of sulfonation as a function of reaction temperature (in the case of the discontinuous laboratory sulfonation of palm kernel fatty acid methyl ester) with a mole ratio of ester:SO_3 of 1:1.3. Temperatures of 70-90 C were required to achieve an adequate degree of sulfonation. The SO_3 reacted exothermically and rapidly with the fatty acid ester at lower temperatures (apparently by adduct formation at the carbonyl oxygen atom of the ester group) without resulting in a large degree of sulfonation. Only at increased temperature can an increased amount of sulfonation take place at the α-C-atom.

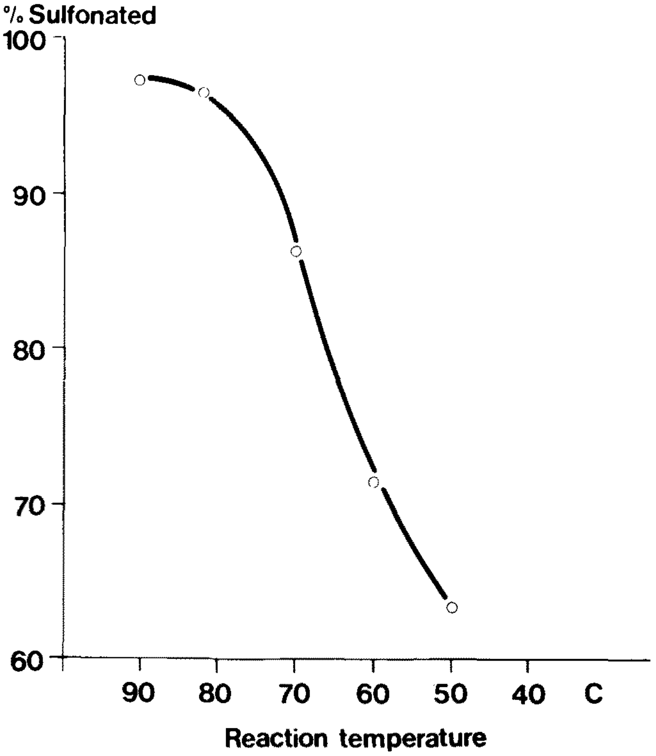


FIG. 1. Sulfonation of palm kernel methyl ester-degree of sulfonation vs reaction temperature. Reaction time = 60 + 10 min; mole ratio = ester: SO_3 = 1:1.3; 5 % by volume SO_3 in air.

The use of temperatures of 70-90 C, however, lead to the unavoidable formation of darkly colored side products. It was shown that lightly colored ES could be obtained by means of a special bleaching process when the side products formation could be held in check by a suitable choice of sulfonation conditions.

To achieve a practical, quantitative sulfonation of the fatty esters, an excess of SO_3 must be used. The amount of SO_3 used has a decisive factor in side product formation, and was dependent upon the sulfonation process used. In the case of discontinuous sulfonation on a laboratory scale, the degree of sulfonation of palm kernel methyl ester as a function of the amount of SO_3 is shown in Figure 2. The necessary excess SO_3 was ca. 30 mole-%. In the case of continuous sulfonations using continuous short time sulfonation reactors, a smaller excess of SO_3 was used. A laboratory thin film reactor required ca. 20 mole-%, and a Chemithon reactor ca. 10-20 mole-% excess. The degree of sulfonation was greater than 97%.

As already mentioned, the sulfonation of fatty esters proceeded in two stages. The first stage was rapid adduct formation between the SO_3 and the ester group. The second stage was the slow, temperature dependent sulfonation in the α-position. Total reaction time to achieve 95% reaction in the case of discontinuous sulfonation was of the order of 50-60 min with a 30 mole-% SO_3 excess at 80 C. In continuous short time sulfonation reactors, the residence

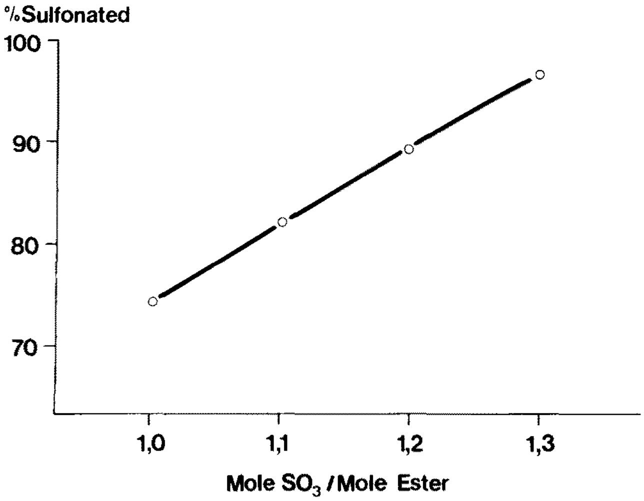


FIG. 2. Sulfonation of palm kernel methyl ester-degree of sulfonation vs SO_3:ester mole ratio. Reaction time = 60 + 10 min; reaction temperature = 80 C; 5 % by volume SO_3 in air.

time of only a few seconds at 80-90 C was not sufficient to achieve a quantitative sulfonation. Therefore, a second reaction stage was used whereby the sulfonated products remained at 80-90 C for 10-20 min.

The most advantageous sulfonation process with respect to color of the sulfonated products and their bleachability, has been shown to be the continuous cascade process. The temperatures during sulfonation were increased from 50 C in the first reactor to 60 C in the second, 70 C in the third, and 80-85 C in the fourth reactor. The SO_3 was distributed in the ratio of 40:20:20:20 in the individual reactors (5). In the case of shorter chain fatty esters, the cascade principle can be altered so that necessary uptake of SO_3 occurs in the first reactor at a temperature of 30-40 C, and the actual sulfonation occurs at 80-90 C in a second reaction step (6). By this means, losses of low boiling, short chain fatty esters by evaporation are avoided.

TABLE II

Bleaching of α-Sulfonated Palm Kernel Ethyl Ester:Color at Various Hydrogen Peroxide Quantities[a]

Hydrogen peroxide quantity (wt %)[b]	Color[c]		
	Yellow	Red	Blue
0	NM[d]	NM	NM
0.5	18.6	3.4	0.5
1.0	7.3	1.0	0.4
1.5	2.5	0.7	0.3
2.0	2.5	0.4	0
2.5	1.9	0.2	0
3.0	1.5	0.1	0

[a] Reaction conditions: bleaching time-2 hrs; temperature = 60 C H_2O_2 concentration = 40 wt-%.

[b] Calculated on the basis of sulfonated product.

[c] 5 wt-% solution; measured by Lovibond 4 in.cell.

[d] NM = not measureable.

TABLE III

Bleaching of α-Sulfonated Palm Kernel Ethyl Ester: Degree of Hydrolysis and Color at Various Hydrogen Peroxide (H_2O_2) Concentrations[a]

Hydrogen peroxide concentration (wt %)	Sulfuric acid concentration (wt %)	Degree of hydrolysis (%)	Color[b]		
			Yellow	Red	Blue
80	94	5	7.0	1.7	0
60	83	8	2.7	0.7	0
40	68	10	2.0	0.3	0
20	44	17	3.1	0.8	0
10	26	36	7.0	1.3	0

[a] Reaction conditions: bleaching time = 2 hr; temperature = 60 C; H_2O_2 quantity = 3 wt-%, calculated on the basis of sulfonated product.

[b] 5 wt-% solution; measured by Lovibond 4 in. cell.

The preparation of bleachable sulfonated products by continuous sulfonation under optimal reaction conditions has been described above. The following technical possibilities were available: (A) Multiple step working conditions such that the reaction vessels are arranged in a cascade sequence with stepwise controlled temperatures and controlled SO_3 additions. This type of reaction procedure is used, for example, in the Ballestra sulfonation plant (7,8). (B) Use of short time sulfonation reactors which operate according to the falling film, thin film, annular space, or injection principle with an additional stage for an extended residence time reactor. In these reactors extensive mixing of reaction components and simultaneous rapid removal of the heat of reaction at the reaction site takes place. This has the effect of reducing the required excess of SO_3, thus keeping the formation of difficultly bleachable side products to a minimum.

Reactors other than the Cemithon reactor (4), which has been successfully used by us, may also be suitable, e.g. the Allied Chemical Co. and the Stepan reactors (7). The quality of the resultant products would be especially good when approaches A and B are combined, i.e. two or three short time reactors connected together.

Fats, i.e. fatty acid triglycerides, after hardening can also be sulfonated under the reaction conditions given. Because the high viscosity of the sulfonated fats caused difficulties in sulfonation, at least 10-25% by wt of fatty acid esters of short chain alcohols, e.g. methyl esters, must be added (9). The esters of alchohols having chains of more than three carbon atoms, and ether alcohols, are cleaved to a large extent during the sulfonation, resulting in a poor yield of ester sulfonates. For the preparation of these types of ester sulfonates in good yields, ca. 50% neutralized α-sulfonated fatty methyl esters are subjected to exchange of ester groups with the desired long chain alcohols or ether alcohols.

Bleaching of α-Sulfonated Fatty Acid Esters

Even when the fatty esters have been sulfonated under

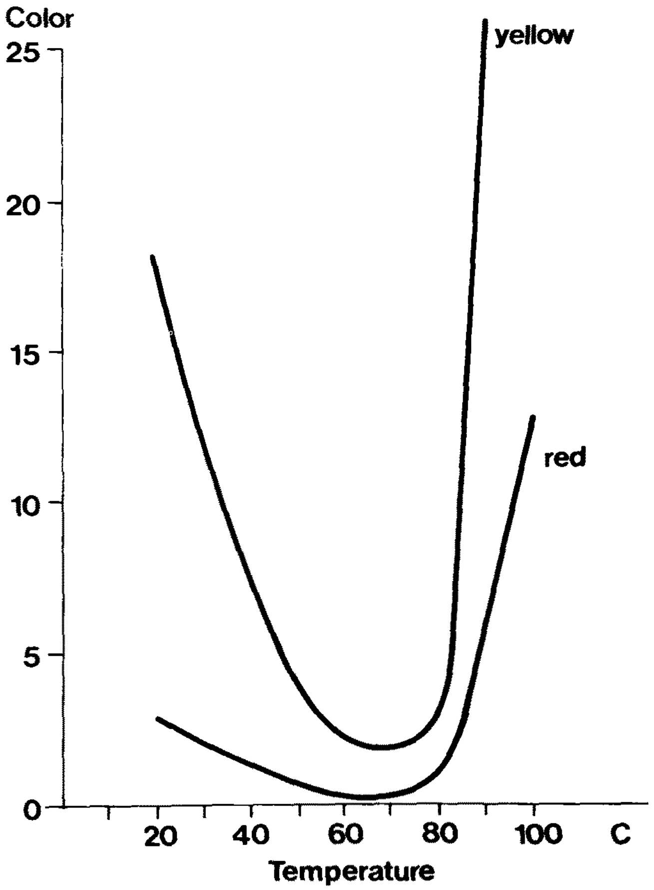


FIG. 3. Bleaching of α-sulfonated palm kernel methyl ester. Bleaching time = 2 hr; 2 wt-% H_2O_2 (40 wt-% solution); Lovibond color; 4 in. cell; 5 wt-% solution.

TABLE IV

Typical Composition and Color Numbers of Ester Sulfonates

Sulfonation method	Ester sulfonate	Color[a] Yellow	Red	Blue	Sulfonate (%)	Unsulfonated matter (%)	Disodium sulfate (%)
Laboratory scale, batchwise	PMS[b]	4.1	0.5	0	39	2.1	4.8
Laboratory scale, batchwise	TMS[c]	9.4	1.8	0	24.5	1.4	2.6
Laboratory scale, continuous	PMS	2.3	0.3	0	40	1.4	2.9
Laboratory scale, continuous	TMS	6.6	1.3	0	24.5	1.0	1.9
Pilot plant, multistep sulfonation	PMS	1.1	0.1	0	39	1.3	4.4
Pilot plant, multistep sulfonation	TMS	4.9	0.9	0	24	0.9	2.4
Pilot plant, 2 in Chemithon reactor	PMS	1.2	0.2	0	39.5	0.8	2.8
Pilot plant, 2 in Chemithon reactor	TMS	5.6	1.0	0	25	0.6	1.8
Production plant, 12 in Chemithon reactor	PMS	2.0	0.2	0	39.6	0.8	2.2

[a] 5 wt -% solution; measured by Lovibond 4 in.cell.

[b] PMS = Palm-Kernel methyl ester-α-sulfonate.

[c] TMS = Tallow methyl ester-α-sulfonate.

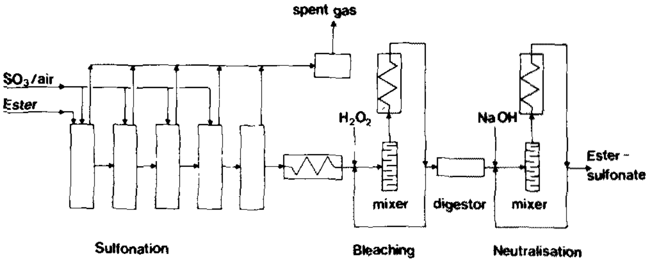


FIG. 4. Flow sheet of the manufacturing process for fatty ester sulfonates.

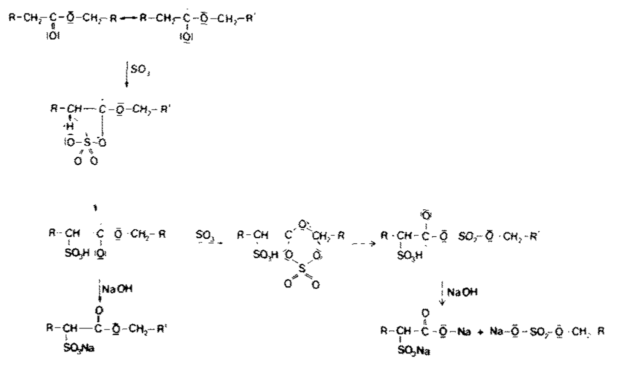


FIG. 5. Reaction mechanism of the α-sulfonation of fatty acid esters. ⟶ = Major reaction; - - -› = minor, side reaction.

optimal conditions, the ES were still dark colored. Conventional bleaching process by addition of sodium hypochloride or hydrogen peroxide to neutralized aqueous solutions of the ES led to products which were totally unsatisfactory because of poor color. Ozone or a bleach under reducing conditions also gave products which possessed poor color properties. We found that the ES could be satisfactorily bleached with H_2O_2 before neutralization attention was paid to the amounts and concentration of H_2O_2, the bleaching temperature, and the bleaching time (10). The H_2O_2 was added incrementally as an aqueous solution to the raw sulfonated product. Efficient stirring and efficient means of removing the reaction heat were provided. The influence of the H_2O_2 quantity on the bleaching effect is shown in Table II. A palm kernel ethyl ester prepared by a discontinuous process and containing 28 mole-% free SO_3 was bleached. The color measurement was carried out in all cases with a Lovibond Tintometer using 5 wt-% ester sulfonate solutions in 4 in. cuvettes. An unbleached product, too dark to be measured, was satisfactorily bleached with 2 wt-% H_2O_2 wt basis of sulfonated fatty ester. The optimum quantity of H_2O_2 was dependent upon the quality of the fatty ester to be bleached. It varied from 1.5-3.5%, calculated as percent of the sulfonated product.

The hydrogen peroxide concentration played a decisive role in the bleaching effect. There was a connection between the bleaching effect and the sulfuric acid concentration in the sulfonated product due to the reaction of the excess SO_3 with the water in the H_2O_2. The formation of persulfuric acids apparently played an important role in the bleaching process. Optimum results were obtained when ca. 60-90% concentration of sulfuric acid was present in the sulfonated product. The amount and concentration of H_2O_2 was calculated taking into account the excess SO_3 used. If the concentration of sulfuric acid formed was too high, attack on the sulfonated product with the concomitant worsening of color occurred. If, on the other hand, the concentration was too low, hydrolytic cleavage of the ester occured. The influence of the H_2O_2 concentration on the bleaching effect is shown in Table III. Three % H_2O_2 was added to an α-sulfonated palm kernel ethyl ester, sulfonated in the laboratory by a discontinuous process. It contained 28 mole-% unreacted SO_3. The best bleaching effect was reached with 40% H_2O_2, which corresponds to a 68% sulfuric acid concentration. Ester hydrolysis at this concentration was very low.

The bleaching effect also was strongly temperature dependent. Figure 3 shows that the lightest color was attained at temperatures between 60-80 C. In order not to exceed these temperatures, the considerable heat of reaction was removed by efficient cooling. Temperature control was very critical. If insufficient heat was removed, the reaction rapidly went out of control, resulting in decomposition of the sulfonation products and irreversible darkening of the product. The bleaching times required at a temperature of 60 C were between 10 min and 1 hr. After this time interval, practically complete bleaching of the sulfonation products had occurred. In individual cases where bleaching with H_2O_2 was insufficient because of the poor quality of the starting materials, products of satisfactory color were obtained by the addition of 0.5 wt-% sodium hypochlorite (basis wt of sulfonated product) added as a 13% aqueous solution to the neutral ester sulfonates at 50 C (11).

Bleaching of α-sulfonated fatty esters was carried out continously in several different ways (12). Thus under the optimal bleaching conditions a vigorous stirring device for mixing α-sulfonated esters with H_2O_2 was used in conjunction with a good heat exchanger. It was efficient also in the case of high viscosity liquids and the heat exchanger was capable of functioning as residence time reactor.

Neutralization of α-Sulfonated Esters

The bleached α-sulfonated esters were neutralized with aqueous sodium hydroxide or other aqueous bases. During the neutralization, the temperature did not exceed 45 C to avoid hydrolysis of the ester groups. An efficient mixing device was used to ensure that rapid mixing occurred to give a mixture which was as homogeneous as possible. Simultaneously, the heat of reaction was efficiently removed. The danger of ester hydrolysis, in a continuous process was small when the pH was automatically controlled between a value of 7.5 and 9. The concentration of the sodium hydroxide solution was chosen so that after neutralization a 40% aqueous slurry of sodium palm kernel methyl ester α-sulfonate (PMS), or ca. 25% aqueous slurry of sodium tallow methyl ester α-sulfonate (TMS) was obtained. Such slurries had a low viscosity and were easily processed further. Typical compositions of products obtained in the various sulfonation devices are given in Table IV.

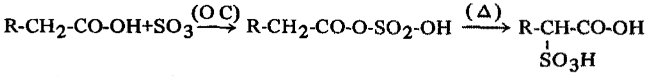
By combining the three steps described (13), sulfonation, bleaching, and neutralization, it was possible to produce ES of perfect quality with degrees of sulfonation greater than 97% when working continuously on a large scale (Fig. 4). The production of ester sulfonates on the basis of palm kernel and coconut methyl esters has been successfully carried out on a 2000 ton/month scale (12 in. Chemithon reactor) over an extended period of time.

Preparation of α-Sulfonated Fatty Acids

The preparation of α-sulfonated fatty acids can be carried out in two ways: (A) By direct sulfonation of fatty acids with SO_3 under the conditions described for the fatty esters. However, sulfonation temperatures were 10-15 C higher, and 1-2% of additional bleach was necessary to attain yields and color quality comparable to those of the esters. Sulfonation of fatty acids with SO_3 in inert solvents also lead to α-sulfonated fatty acids of good quality (14) ("Armosul," Armour Industrial Chemical Co., Chicago, Ill. [15]). However, the use of solvents makes this process quite laborious. (B) By hydrolysis of α-sulfonated esters. The preparation of α-sulfonated fatty acids or their salts was achieved by in process hydrolysis of ester sulfonates. One can either acid hydrolyze the unneutralized α-sulfonated esters by heating them with water, or, preferably, carry out an alkaline hydrolysis of the alkali salts of an α-sulfonated ester with an aqueous solution of the corresponding base at higher temperatures.

Reaction Mechanism for Sulfonation of Fatty Esters

The primary reaction product, resulting from the reaction of fatty acids and SO_3 has been described by de Boer (16) as a mixed anhydride, which rearranges at higher temperatures to an α-sulfo-fatty acid.



$$R\text{-}CH_2\text{-}CO\text{-}OH + SO_3 \xrightarrow{(0\ C)} R\text{-}CH_2\text{-}CO\text{-}O\text{-}SO_2\text{-}OH \xrightarrow{(\Delta)} \underset{SO_3H}{R\text{-}CH\text{-}CO\text{-}OH}$$

On the basis of our experiments, however, we assume the following reaction mechanism for the sulfonation of fatty

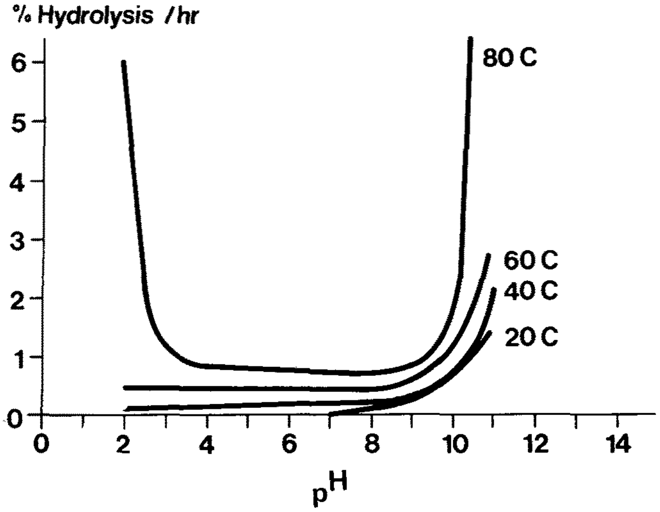


FIG. 6. Rate of hydrolyses of palm kernel methyl ester sulfonate. Concentration = 3.4 g/liter.

TABLE V

Solubility of Sulfonates

Surfactant	Krafft point (C)[b]
Alkylbenzenesulfonate (LAS) ($C_{10\text{-}13}$)[a]	<0.0
Tallow methyl ester sulfonate (TMS) ($C_{16\text{-}18}$)	39.0
Palm kernel methyl ester sulfonate (PMS) ($C_{12\text{-}14}$)	<0.0
α-Olefinesulfonate (AOS) ($C_{15\text{-}18}$)	23.5
Alkanesulfonate (AS) ($C_{14\text{-}17}$)	<0.0

[a] Length of alkyl chain.

[b] Temperature at which 10 g/liter is soluble.

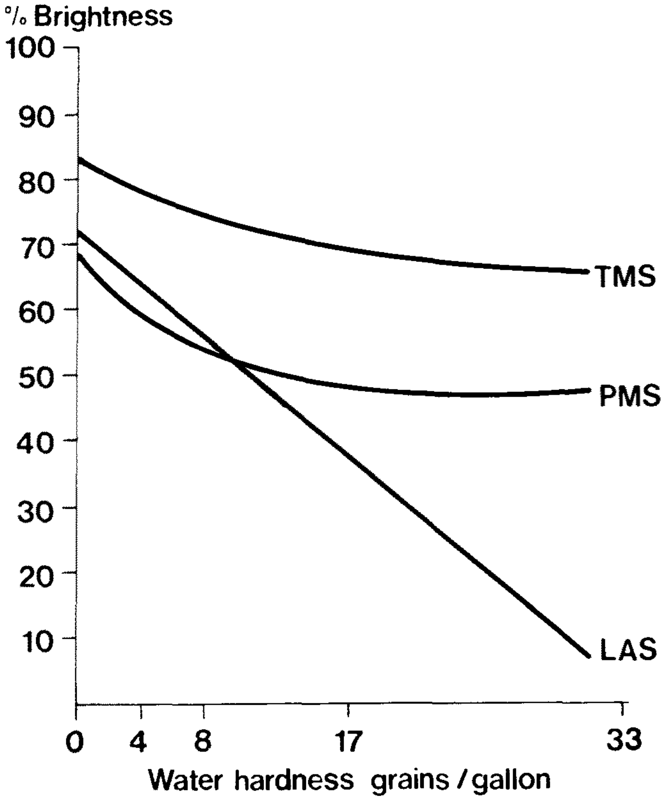


FIG. 7. Effectiveness of washing wool as a function of the water hardness. Temperature = 30 C; washing bath = 1:50; washing time = 15 min; concentration = 2 g product/liter (¼ surfactant + ¾ Na_2SO_4). TMS = Tallow methyl ester sulfonate; PMS = palm kernel methyl ester sulfonate; and LAS = alkylbenzenesulfonate.

TABLE VI

Wool Detergency Tests[a] of Light Duty Detergent Formulations[b]

Surfactant[c]	Concentration (g/liter) 2	4	6
TMS	78.5	85.0	83.0
PMS	63.0	73.5	75.0
LAS	60.0	84.0	85.0

[a] Values expressed as % brightness.

[b] Formulation: 26.5% surfactant, 15.0% sodium tripolyphosphate 50.0% sodium sulfate, up to 100% with other compounds and water; washing bath = 1:50; temperature = 30 C; water hardness = 300 ppm CaCO$_3$/gallon.

[c] TMS = Tallow methyl ester sulfonate; PMS = palm kernel methyl ester sulfonate; LAS = alkylbenzenesulfonate.

TABLE VII

Washing-Tests in the Launder-O-Meter With and Without Tripolyphosphate[a]

Textile	Nonfinished cotton			Finished cotton			Polyester/Finished cotton		
Washing temperature	90 C			90 C			60 C		
Concentration (g/liter)	0.75[b]	2[c]	6[c]	0.75[b]	2[c]	6[c]	0.75[b]	2[c]	6[c]
Surfactant[d]									
LAS	40.4	66.0	76.0	43.6	47.5	73.5	38.4	43.0	60.0
TMS	61.7	72.0	76.0	58.7	51.5	73.0	57.5	45.0	60.0
PMS	46.4	64.0	76.0	53.0	49.0	74.0	50.9	42.5	58.0

[a] Values expressed as % remission; water hardness = 300 ppm CaCO$_3$/gallon.

[b] Anionic surfactant only, without tripolyphosphate.

[c] Formulation: 7.1% anionic surfactant, 2.4% nonionic surfactant, 38.8% tripolyphosphate, up to 100% with complexing agents, sodium perborate and foam inhibitors.

[d] LAS = Alkylbenzenesulfonate; TMS = tallow methyl ester sulfonate; PMS = palm kernel methyl ester sulfonate.

TABLE VIII

Biological Properties of Fatty Methyl Ester Sulfonates and Fatty Acid Sulfonates

Surfactant[a]	PMS	TMS	PAS	TAS
Biodegradibility[b]	94	95	94	93
Acute oral toxicity[c]	3.8	>2.7	>2.2	>2.3
Skin compatability[d]	NR[e]	NR	NR	NR

[a] PMS = Palm kernel methyl ester sulfonate; TMS = tallow methyl ester sulfonate; PAS = palm kernel acid sulfonate; TAS = tallow acid sulfonate.

[b] Organization for Economic Cooperation and Development-Confirmatory test (% decrease in methylene blue active substance [MBAS] after 30 days).

[c] Male, white mice; LD$_{50}$, g/kg body-wt.

[d] Hairless mice, treated once daily for 7 days.

[e] NR = no reaction.

esters. In the first stage, the SO_3 reacts in the extreme canonical form, which carries a positively charged sulfur atom with the free electron pair of the carbonyl oxygen of the ester group. Due to the increased activation of the α-hydrogen atoms because of adduct formation, a rearrangement then occurs, whereby an α-hydrogen atom is substituted by an SO_3 group forming a C-S bond (Fig. 5). A minor side reaction occurs which requires additional SO_3. This reaction is apparently the formation of an anhydride from sulfocarboxylic acid and alkyl sulfuric acid which is easily cleaved by alkali. This side reaction becomes the major reaction in the case of fatty esters of longer chain alcohols.

Properties of Fatty Acid Sulfonates and Ester Sulfonates

Chemical properties: The hydrolytic stability of the ES is of great practical importance. The ester group apparently is stabilized markedly by the α-sulfonate group. This is shown in Figure 6. The hydrolysis rate of PMS is plotted as a function of temperature and pH at a concentration of 3.4 g PMS/liter, i.e. a concentration which corresponds to concentrations in a washing solution. The hydrolysis rate of the ES is very slow, in the pH range of 3-9.5 even at temperatures of 80 C. The product is stable in a neutral detergent solution, and minimal hydrolysis has been found during spray drying of a PMS containing detergent slurry, and after storing neutral solutions of the ES at 60 C for several months.

Physical properties: In general, one can say that ES of short chain alcohols possess excellent washing properties, whereas, the ES in which the sulfonate group is in the middle of the molecule (as in the case of long chain alcohol esters), possess good wetting, but poor washing properties (17). Optimum washing properties are reached in the case of the methyl ES with C_{16}-C_{18} fatty acids. In the following text we concentrate mainly upon the properties of the technically important methyl ES (sodium salts) on the basis of palm-kernel oil (or coconut oil) (PMS) and tallow (TMS).

The solubility of a series of sulfonates is shown in Table V and expressed as Krafft-Points. TMS was clearly much less soluble than alkylbenzenesulfonate (LAS). The ES, especially TMS, in contrast to LAS possess detergency which was independent of water hardness. This is shown in Figure 7 in which the washing power for wool in the absence of complexing agents is shown as a function of water hardness. When TMS was used in a light duty detergent formulation its excellent washing properties become apparent, especially at low concentrations (Table VI). TMS washed noticeably better than PMS, but PMS had better foaming properties (up to 40 C). Launder-o-meter washing tests with heavy duty detergent formulations containing ES, using finished and nonfinished cotton as well as polyester-cotton blends, further demonstrate the good washing properties of TMS even at low concentrations as shown in Table VII. It should be noted that TMS possessed good washing properties for cotton and polyester-cotton blends in the absence of tripolyphosphate. This was not the case with LAS. The reason for this and for the good washing properties at low concentrations was probably due to the low sensitivity of TMS to water hardness. Therefore, TMS is especially interesting for the development of low phosphate or phosphate-free washing and cleaning agents. It should be mentioned, however, that problems concerning secondary properties still exist, such as fabric incrustation in the complete absence of phosphates. The soil suspending power of TMS was also satisfactory.

A disadvantage of TMS containing detergents, when used in the normal European horizontal drum type automatic washers is that they have a tendency to produce too much foam due to the extensive mechanical action. In the U.S., these difficulties may not appear, however, due to the different type of construction of the washing machines and the lower washing temperatures. The use of special foam inhibitors, or the addition of other detergents may solve the problem of too much foam with TMS containing washing formulations, even in drum type automatic washers. Such problems were not encountered with PMS.

The disodium salts of sulfonated palm kernel fatty acids and sulfonated tallow fatty acid possess markedly lower solubility than the corresponding ES. Furthermore, they are inferior in their washing power compared to ES and LAS.

The viscosity of aqueous solutions of other surfactants, e.g. alkylbenzenesulfonates, soaps, alkyl sulfates, alkylethersulfates, and ES can be lowered markedly by the addition of the disodium salts of FAS (especially C_{10}-C_{12}) (18-20). The preparation of such low viscosity surfactant solutions is important in the case of liquid washing and cleaning agents, and for the preparation of detergents slurries which are to be spray dried as laundry detergents. Detergent slurries containing ES can be spray dried to washing powders possessing adequate powder properties. The presence of disodium salts of FAS improves the powder properties further. The properties of detergent powders containing other surfactants, e.g. alkyl benzenesulfonates, alkane sulfonates, olefin sulfonates, alkylsulfates, alkylethersulfates, and alcohol polyglycol ethers, can be optimized similarly by the addition of the disodium salts of FAS (21-23). However, ES are not only of interest as raw materials for washing products. TMS is described in the literature as being a good lime soap dispersing agent (24). ES are suitable for the antistatic finishing of fibers (25). Special ES and FAS can also be used as release agents for rubber and polyurethane elastomers (26-28). FAS possess good properties as emulsifiers for the emulsion polymerization of PVC (29-31). Special ES with alkylpolyglycol ethers have been used as constituents for spin finish agents used with synthetic fibers (32). ES and FAS with double bonds that have been chlorinated, possess good properties as leather auxiliaries (33). ES can also be used in cosmetic preparations, as surfactants in toothpastes and shampoos, as well as in many other areas of application.

Biological properties: ES and FAS can be degraded biologically easily, possess a low acute oral toxicity, and good skin compatibility. The data for the biological properties are shown in Table VIII.

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