



Summary of the Technology for the Manufacture of Higher Alpha-Sulfo Fatty Acid Esters¹

B.L. KAPUR, J.M. SOLOMON, and B.R. BLUESTEIN, Technical Center, Witco Chemical Corporation, Oakland, New Jersey

ABSTRACT

Interest in α -sulfonated higher molecular weight (up to C_{20}) fatty esters has increased in recent years in the surfactant industry due to the advent of economical sulfonation processes and methyl esters of fatty acids. In this paper, the authors present a review of the chemistry of the sulfonation of fatty esters and the two-step mechanism leading to α -sulfonation. Laboratory and pilot plant scale preparation of long chain fatty acid α -sulfoesters with vaporized SO_3 without the use of solvents are also summarized. Work on the falling film equipment with hydrogenated methyl tallowate with vaporized SO_3 is described along with procedures for neutralization and bleaching. Analytical methods for defining the α -sulfonates are discussed. A larger scale unit to continuously manufacture α -sulfo fatty esters from long chain fatty acid is described. A review of the commercially available continuous processes for sulfonation of the fatty acid esters with vaporized sulfur-trioxide have also been included. The properties of the salts of α -sulfo fatty esters including the hydrolytic stability, aqueous solubility, lime soap dispersing ability, and biological properties have been tabulated. Uses of these surfactant range α -sulfo esters are included in this discussion.

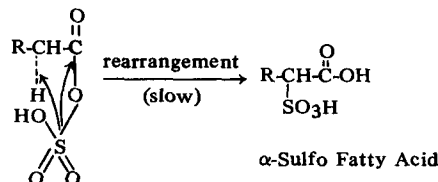
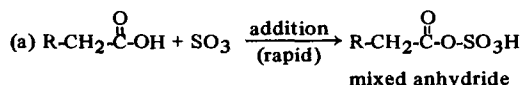
INTRODUCTION

This paper is a summary of the technology for the manufacture of sodium α -sulfo methyl tallowate with its excellent detergent and lime soap dispersing properties, high levels of biodegradability, and low toxicity which is of current interest because these products are being manufactured in Japan (1-4). Although the sulfonation of fatty acids generally has been carried out over a period of several decades, it is only in the past 10-15 years that advances (i.e., availability of stabilized liquid SO_3 , high purity tallow fatty acid esters, and continuous thin film equipment) have been made in sulfonating long chain fatty acid esters culminating in the recent construction of a plant for the production of α -sulfo tallow esters. Earlier background laboratory work before this recent commercialization was done in the United States at the Eastern Regional Research Center of the U.S. Department of Agriculture and in Germany at Henkel and Cie. It is important to note that a serious attempt at commercialization was made in the mid 1960s by Stepan Chemical Co. This survey also includes our unpublished work on the continuous direct sulfonation of saturated fatty acid esters with sulfur trioxide in a turbulent falling film reactor. The chemistry of the preparation of α -sulfo fatty acid esters includes the reaction mechanism of α -sulfonation of the higher fatty acid esters as well as procedures for the neutralization and bleaching of the sulfonated fatty acid ester. Reference is made to a process for manufacture of α -sulfo fatty acids or esters and also described is the availability

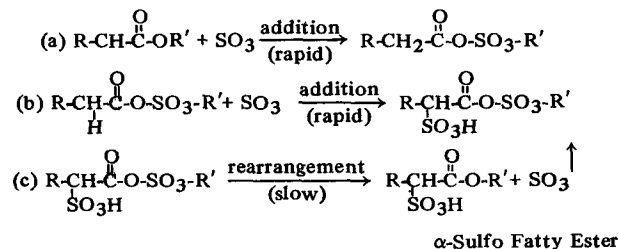
of industrial sulfonation equipment. Finally, the properties of the α -sulfo tallow esters which include biodegradability, hydrolytic stability, and biological compatibility generally are examined in detail. Because these products have a unique combination of desirable properties, their use in detergent powders, liquid formulations, and detergent bars should see a many-fold increase in the near future.

REACTION MECHANISM FOR α -SULFO FATTY ACIDS AND ESTERS

A mechanism for the α -sulfonation of saturated fatty acids with sulfur trioxide has been proposed by deBoer (5). He mentions the initial formation of a mixed anhydride. This is similar to the mechanism reviewed by Watson (6) for α -bromination of fatty acids to form the acid bromide as an intermediate. Stirton (7) reviewed the sulfonation mechanism in terms of the reaction of long chain fatty acids with sulfur trioxide. The mechanism was proposed as two steps in the sulfonation procedure: (a) formation of mixed anhydride and (b) rearrangement of the mixed anhydride at a higher temperature to form the α -sulfo fatty acid. Schematically they are shown below.



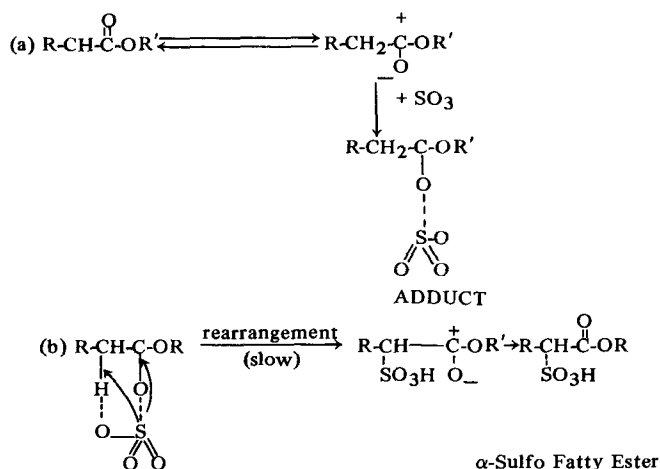
The mechanism of sulfonation of long chain fatty esters with SO_3 was studied by Smith and Stirton (8), and on the basis of their experimental work they concluded that the first step is the formation of a complex between the saturated fatty ester and SO_3 . This complex activates the α -hydrogen which is susceptible to attack by a second molecule of SO_3 . This intermediate rearranges and allows SO_3 to be lost prior to neutralization over a period of time, at room or elevated temperature as follows:



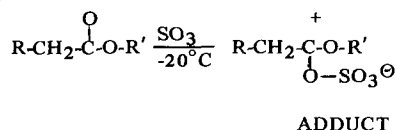
A slightly different form of the above mechanism for the α -sulfonation of the higher fatty esters is discussed in a paper by Stein et al. (9,10). They also propose two stages in their mechanism; the first stage being the addition of SO_3 to the carbonyl oxygen of the ester, which is a rapid

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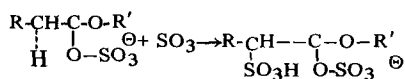
reaction. This adduct activates the α -H atom, and in the second stage rearrangement occurs to form the α -sulfo fatty ester.



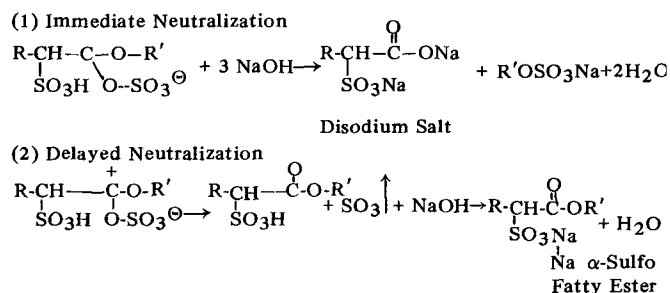
Recently, Nagayama et al. (11) (Lion Fat & Oil Co. Ltd) have followed the reaction of α -sulfonation of the higher fatty esters using nuclear magnetic resonance. They observed the presence of two intermediates in the formation of α -sulfo ester. The first intermediate was formed by addition of SO_3 to the carbonyl oxygen at low temperature.



This adduct activates the α -hydrogen of the fatty ester and then a second mole of SO_3 is attached to give the second intermediate.



Then, if neutralization is immediate, the disodium salt is formed. However, if neutralization of the acid is delayed, the α -sulfo ester monosodium salt is obtained as shown below.



This still does not explain the reformation of the ester by delayed neutralization. As pointed out by Smith and Stirton (8), the mechanism leading to the reformation of ester is not known, but the overall process seems to involve a rearrangement to lose SO_3 prior to neutralization.

PROOF OF STRUCTURE FOR SULFONATION IN THE α -POSITION

The evidence that sulfonation with sulfur trioxide takes place on the α -position, rather than the β - or γ -position, with the higher molecular weight fatty acids, has been demonstrated by Weil et al. (12). Three routes were chosen

by Weil to establish the sulfonation in the α -position. The routes were:

- A. Sulfonation \rightarrow Bromination \rightarrow Amidation
 B. Bromination \rightarrow Amidation
 C. Bromination \rightarrow Conversion to mercaptan \rightarrow Oxidation \rightarrow Bromination \rightarrow Amidation

They used palmitic acid as the fatty acid. The final products obtained by the three routes had identical melting points and X-ray diffraction patterns. Therefore, they concluded that sulfonation of the higher saturated acids is specific and leads only to monosulfonation.

RAW MATERIALS

Higher Fatty Acid Esters

The straight chain and saturated monocarboxylic acids referred to in this summary are in the range of C_{10} to C_{20} and in particular C_{12} (lauric), C_{14} (myristic), C_{16} (palmitic), and C_{18} (stearic) acids because of their application in the surfactant industry. These acids are derived from coconut oil and animal fat. Since the recent availability of the higher molecular weight methyl fatty esters (13,14), these esters have drawn more attention both from a processing and application point of view. Fatty acid esters are derived from both mono- and polyalcohols. Stirton and co-workers (15) have prepared several different types of esters. These include esters of linear and branched chain, primary and secondary alcohols (ranging from 1-18 carbon atoms), and representative ring compounds to study the relationship of structure with useful properties. Recently, Weil et al. (16,17) prepared monoesters of polyhydric alcohol and of hexitols and sucrose in their search for effective detergents and lime soap dispersing agents. Further work by these authors (18) has been the change of the cation from the standard Na to Li, NH_4 , K, Mg, and Ca and also ethanolamines to further study the structure-surfactant property relationship.

Sulfonating Agents

The sulfonating agents which have been used for α -sulfonation of long chain fatty acids are (a) stabilized liquid SO_3 , (b) sulfur trioxide vapor, (c) chlorosulfonic acid, and (d) dioxane-sulfur trioxide complex. Stirton et al. (19) have used liquid SO_3 extensively for batch sulfonating the fatty acids in a solvent system. They also did some work with vaporized sulfur trioxide on semiliquid fatty acids (7). More recently, Stein et al. (20-22) have used vaporized SO_3 in pilot plant equipment for sulfonating long chain fatty acid esters. With the advent of commercial advances in continuous sulfonation-sulfation equipment using vaporized SO_3 , the trend has been to sulfonate fatty acid esters with vaporized SO_3 (23). Chlorosulfonic acid was used by Guenther (24) and Bert (25) in the same way as liquid SO_3 . However, higher temperatures were required to give yields comparable to those obtained with liquid SO_3 . Also, the higher temperatures caused the resultant product to be dark colored. There is no advantage to the use of chlorosulfonic acid. In fact, the higher cost of the acid and the production of the corrosive by-product HCl are disadvantages. The dioxane-sulfur trioxide complex with fatty acids has given lighter colored products with high yield as reported by Ishiguro et al. (26). This complex has also been found useful in avoiding ring sulfonation and decomposition in the preparation of α -sulfonates in the presence of an aryl, hydroxyl, or chloro group in the hydrocarbon moiety according to Weil et al. (27).

SMALL SCALE SULFONATION OF FATTY ACID ESTERS

Laboratory and Pilot Plant Scale Preparation of Long Chain Fatty Acid α -Sulfo Esters

With the availability of essentially pure commercial fatty acids and stabilized liquid SO_3 , active interest in the α -sulfonation of fatty acids and esters was undertaken by (a) A.J. Stirton and co-workers in the U.S.A., (b) W. Stein and co-workers in Germany, and more recently by (c) Lion Fat & Oils Ltd. in Japan (26).

Preparation of α -Sulfo Fatty Acid Ester via α -Sulfo Fatty Acids

Stirton et al. (19) have reported the α -sulfonation of saturated fatty acids from lauric (C_{12}) to behenic (C_{22}) acids with liquid sulfur trioxide. High yields of dark colored products were obtained by the dropwise addition of 1.5-1.7 molar ratio of SO_3 to the fatty acid dispersed or dissolved in chloroform, carbon tetrachloride, or tetrachloroethylene. The reaction temperature was increased to 65 C in the final stages of sulfonation and maintained for 1 hr. The reaction mass was cooled, filtered, and the filter cake was washed with cold solvent and dried. The yield of the α -sulfonated acid was 75-85%.

The esterification was carried out with either the α -sulfonic acid alone in which the free sulfonic acid served as its own catalyst or by using the monosodium salt and a mineral acid catalyst (15,28).

While esters of α -sulfo fatty acids have been successfully prepared in a pure state by esterification of α -sulfo acid or its monosodium salt, limited attention to the direct sulfonation of long chain fatty esters with sulfur trioxide is found in the literature.

Moyer in 1940 (29) reacted methyl esters of hydrogenated coconut oil and tallow with liquid SO_3 (distilled from oleum) in the presence of liquid SO_2 , under pressure, at 25 C and substantially anhydrous conditions for a period of 24 hr. After neutralization, the product obtained was the disodium salt of sulfonated fatty acids. This indicated ester cleavage either during sulfonation or neutralization. Smith and Stirton (8) undertook to sulfonate pure lower alkyl esters of palmitic and stearic acid with liquid SO_3 with mainly CCl_4 or without solvent at 0 C. Both Moyer (29) and Smith and Stirton (8) used a high molar ratio of SO_3 /fatty ester 3:1 and low temperatures for the addition of liquid SO_3 . Stirton also found that at 1:1 molar ratio of SO_3 /fatty ester there was no sulfonation. However, with reaction at the higher molar ratio, Stirton also found that upon *immediate* neutralization of the sulfonated product, the final product was the α -sulfonated disodium salt. Nevertheless, if the reaction mixture was allowed to remain at room temperature or heated to 60 C for some period of time (at least 1 hr) and carefully neutralized, the then final product contained 60% α -sulfonated ester. Stirton's experimental work demonstrated that the equilibration time, at elevated temperatures after addition of SO_3 was very important if α -sulfo ester was to be the desired product. This indicated that ester cleavage essentially took place in the sulfonation step. The sulfonation of fatty esters with vaporized SO_3 is dealt with in the next section.

Direct Continuous Sulfonation of Higher Fatty Esters with Vaporized SO_3

The work of Stein et al. (20-22) over the past decade has dealt with the sulfonation of fatty acid esters using diluted vaporized SO_3 without solvent. They used vaporized SO_3 diluted with air. The apparatus for sulfonation consisted of five vessels arranged in tandem and referred to as a

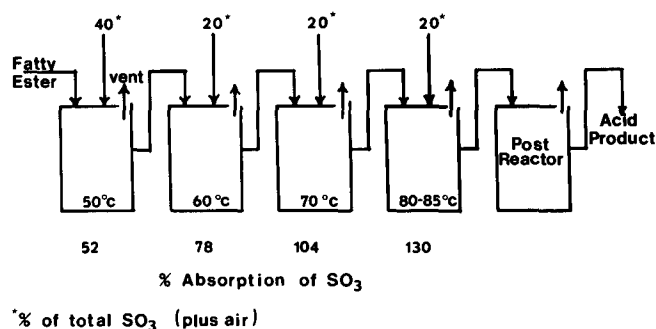


FIG. 1. Cascade apparatus for α -sulfonation.

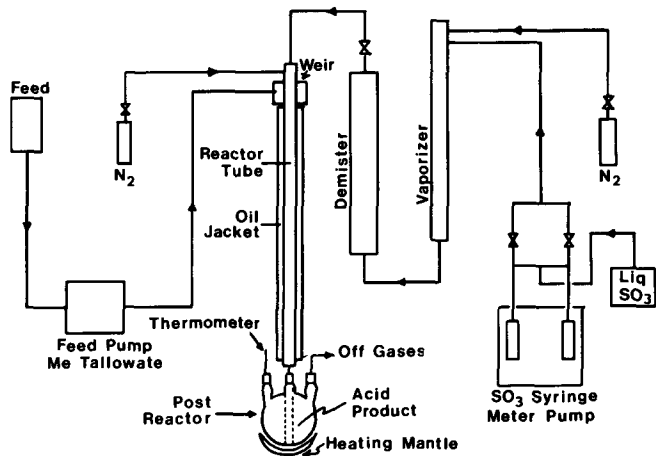


FIG. 2. Laboratory continuous thin film sulfonation reactor.

continuous cascade type reactor. The concept of this design was similar to batch sulfonation with an overflow to attain continuity. Using this reactor system it was also possible to sequentially add diluted SO_3 and thereby obtain a lighter colored product because "burning" with excess SO_3 is avoided. Figure 1 shows the flow diagram of this system. The final molar ratio of SO_3 /fatty ester was 1:3, and the SO_3 was diluted to 5 vol % in air.

Direct Continuous Sulfonation of Hydrogenated Methyl Tallowate with Vaporized SO_3 in a Falling Film Reactor

A continuous thin film laboratory reactor has been used for the sulfonation of hydrogenated methyl tallowate at the Witco Technical Center in Oakland, NJ. The basis for the construction of this reactor was a paper by Hurlbert et al. (30,31). A flow diagram of this modified continuous laboratory thin film reactor system is shown in Figure 2, and the details of the reactor head are shown in Figure 3. The reactor head was constructed so that there were three inlets. The first inlet (A) is for the carrier gas (air or nitrogen). The carrier gas picks up the liquefied hydrogenated methyl tallowate as it flows from the second inlet (B) over a weir and carries it as a turbulent liquid film downward along the reactor wall into the reaction zone. A second stream containing vaporized SO_3 enters at the third inlet (C).

The organic feed and the diluted gaseous SO_3 then cocurrently enter a jacketed reactor (10 mm ID and 55 in. long). Where the two streams meet, turbulence occurs and sulfonation is initiated. For most organic species the reaction is completed in the length of the reactor; however, in the case of α -sulfonation a post residence period is required. The sulfonation of hydrogenated methyl tallowate is described in the following section.

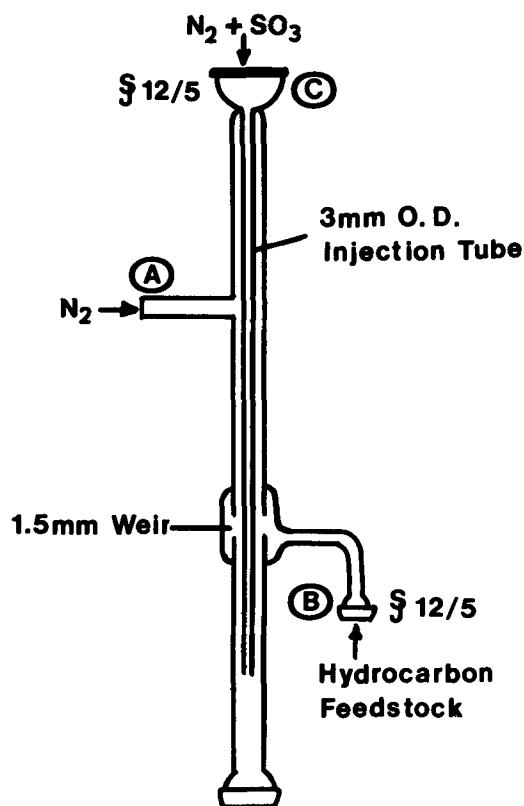
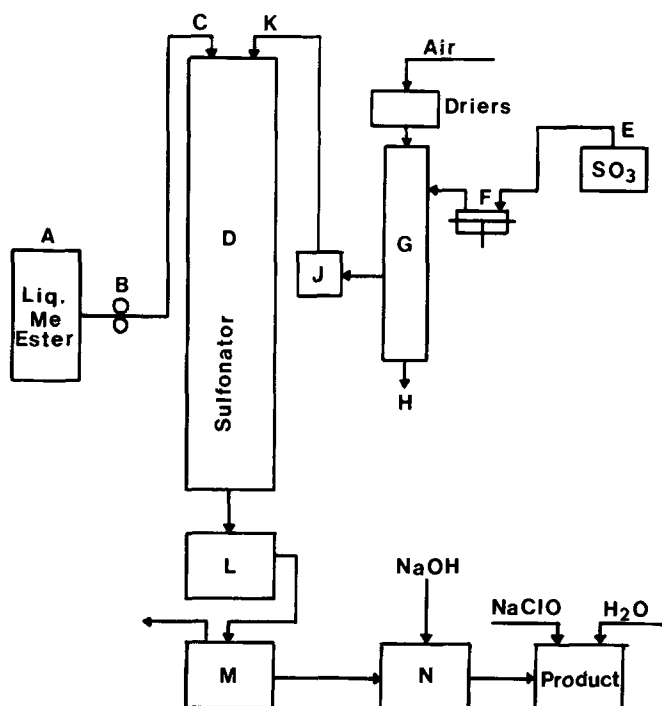


FIG. 3. Detail of reactor head.

FIG. 4. Flow diagram for manufacture of sodium α -sulfotallow ester.

Sulfonation

Hydrogenated methyl tallowate (Emery's filtered Metholene 2204), maintained at 45-50 C in a flask, was metered by a gear pump to a weir located on the head of the oil jacketed reactor (ID 10 mm). The inlet temperature of the hydrogenated methyl tallowate and the oil temperature of

the jacketed reactor (55 in. long) were each maintained at 82-85 C. Liquid SO_3 was metered using syringe pump into the electrically heated vaporizer and then passed through a demister into the reaction zone of the jacketed reactor. A dry N_2 stream was split between the vaporizer and the reactor tube. The methyl tallowate formed a film on the wall of the reactor tube where it was exposed to the dilute (11 vol %) SO_3 vapor. The reactor effluent was collected (over a 45 min period) in a receiver maintained at 75-85 C to provide adequate sulfonic acid- SO_3 contact after which the product was purged with dry N_2 to eliminate absorbed SO_3 .

Neutralization and Bleaching

Batch neutralization of the effluent mixture sufficient to prepare about 35% active sodium salt was carried out in high shear equipment (e.g., Hobart mixer) by adding the liquefied acid product (about 50 C) to a predetermined quantity of water (based on 85% α -sulfo ester in the acid mix). A 30% aqueous solution of sodium hydroxide was then added in small increments with constant mixing of the resultant paste. Finally, the neutralized product was bleached to a light yellow color with 3-4 wt % NaOCl (15 wt % solution).

Engineering — Process (Overall) in Unit Operation

A large scale unit to continuously manufacture α -sulfonates from long chain fatty acids or esters has been proposed. Figure 4 is a flow sheet for the manufacture of fatty ester sulfonate.

Liquefied methyl ester (A) was fed through a metering pump (B) to the top (C) of the stainless-steel jacketed sulfonator (D) which was maintained at 80 C. Liquid SO_3 (E) was metered through a diaphragm pump (F) to the vaporizer (G) which has a drain (H) to allow removal of accumulated SO_3 -stabilizer and H_2SO_4 residue. The mole ratio of SO_3 /methyl ester was adjusted between 1.2-1.4. The vaporized SO_3 was diluted with dry, compressed air, to a level of 5-10 vol % and swept through trap (J) (to trap entrained liquid droplets) to the top of the sulfonator (K). The liquefied methyl ester falls as a thin film (by means of a weir) where, on contact with air- SO_3 sulfonation takes place in a turbulent film. The product has had a relatively short residence time in the sulfonator (D) has not had adequate time for the completion of the reaction. Therefore, the product was passed through a stainless-steel post reactor (L) where a residence time of 15-20 min at 80 C completes the reaction (95-97% conversion). Next it was passed into a disengaging vessel (M) to remove unreacted SO_3 . The warm sulfonic acid was continuously neutralized (N) with 30% aqueous NaOH to a pH of 7.5 to 11, to prevent ester hydrolysis and finally adjusted to a 30-40% active with water. To improve the color of the product, it was bleached with sodium hypochlorite solution (3-4%) to obtain a product 30-35% active. The hypochlorite bleach can be added during or after neutralization.

COMMERCIAL SCALE SULFONATION EQUIPMENT

Potential Manufacturing Sulfonation Techniques

Some of the more important elements of any SO_3 sulfonation process is (a) the way in which the reactants make contact, (b) how the exothermic heat of reaction is removed, and (c) how the reaction product is protected from decomposition to avoid undesirable dark colors. Therefore, a brief description of the principles employed in the commercially available continuous processes are reviewed.

Ballestra's Process

In 1963 Ballestra (32) published a review of his continuous sulfonation process. The process consisted of a series of batch-type reactors combined to attain a continuous flow. Some Ballestra systems used as many as five sulfonators. The organic reactant and the diluted SO_3 gas stream entered parallel into the first reactor. Special high speed turbines dispersed the SO_3 gas and organic reactants. The concentration of SO_3 in the gas stream was decreased as the sulfonated mixture passed from one reactor to another. This technique of sulfonation was claimed to have facilitated the heat transfer resulting in a better product color.

Stepan (23), Allied (33), and Chemithon (34) Continuous Sulfonation-Sulfation Processes

All of the three processes are based on the utilization of a thin-falling film for the organic feed. The sulfonating agent, vaporized SO_3 is diluted with compressed dry air and mixed prior to reaction. Both the reactants are fed to the equipment in a cocurrent stream. The SO_3 reacts with the organic component to form the sulfonic acid which continues through the reactor and is finally disengaged from the residual inert gas using a cyclone type separator. The reaction is therefore characterized as a "single pass" short reaction time process. The differences in the three systems are the way the film is formed and how much turbulence is generated by the mixing of the two reactants during sulfonation. The three reactor heads are illustrated in Figure 5 (Stepan), Figure 6 (Allied), and Figure 7 (Chemithon). The continuous air- SO_3 equipment was designed for sulfonation or sulfation of detergent range alkylbenzene, alcohols, ethoxylated alcohols, and α -olefins. Recently Stein (10) had mentioned that Stepan and Allied type reactors have been successfully used as a 2 in. (pilot) and 12 in. (commercial) Chemithon reactor for the production of α -sulfo fatty esters. The only fatty esters mentioned by Stein et al. for large scale manufacture were the palm-kernel and coconut methyl esters. However, Stepan Chemical Co. (37) in the 1960s made the Biodet and Bioterge series of α -sulfo fatty esters. The Biodets were labeled α -sulfo methyl myristate and the Bioterges, α -sulfo methyl tallowate.

Neutralization, Bleaching, and Analysis of α -Sulfo Ester

Stein et al. have devoted considerable attention to the bleaching of the acid prior to neutralization and have obtained a number of patents (20-22) on this subject (9,10). They used H_2O_2 as the bleaching agent, and emphasized the importance of the following variables: (a) quantity of bleach, (b) concentration of H_2O_2 , (c) bleaching temperature, and (d) time. They found that 3 wt % H_2O_2 (based on sulfonated fatty ester) of a 40% conc. solution at 60 C for 2 hr, with efficient stirring, was adequate to give the best results for bleaching. They also mention a 10% hydrolysis of the ester in the bleaching step, depending on the concentration of sulfuric acid formed with the H_2O from H_2O_2 and excess SO_3 present in the acid mixture. If the H_2SO_4 concentration was too high, the hydrolysis was low, but the color darkened. If the H_2SO_4 concentration was too low, then bleaching occurred, but the hydrolysis of the ester increased. This reflected a very delicate balance to get the maximum bleaching effect and minimum ester hydrolysis.

Other workers have discussed the importance of obtaining light colored products, some of which have been prepared under manufacturing conditions. Stirton and co-workers (15,38) who prepared their α -sulfo esters by direct sulfonation and by esterification of the acid, purified by recrystallization to a white powder.

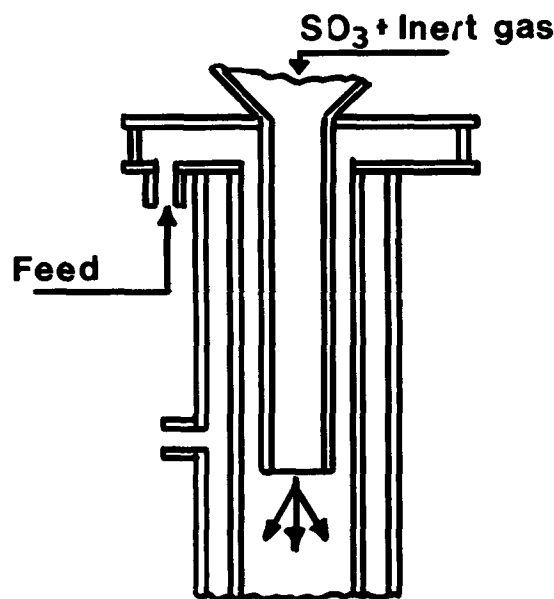


FIG. 5. Stepan's SO_3 sulfonation reactor.

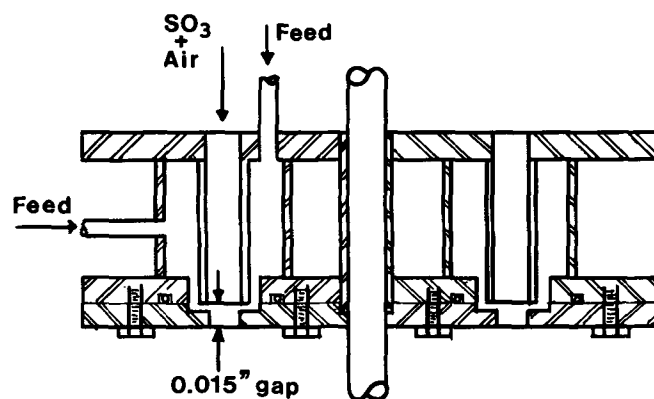


FIG. 6. Allied Chemical Corp.'s reactor head.

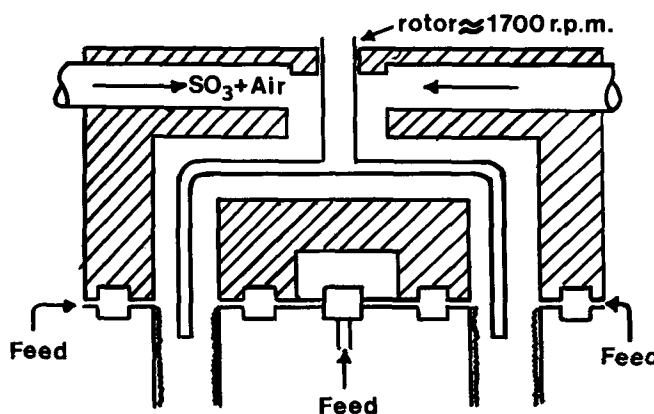


FIG. 7. Chemithon's reactor head.

Neutralization

Both Stein (9) and Stirton (38) have mentioned that the esters are surprisingly resistant to alkaline hydrolysis. They attributed this to the presence of the sulfo group which helped stabilize the ester linkage. Stein conducted his hydrolysis study with a solution of 3.4 g of ester sulfonate per liter of aqueous solution and found that the percentage of hydrolysis per hour was less than 0.5% over a pH range

TABLE I

Salts of Esters of α -Sulfo Fatty Acids, Rate Constants, Acid and Alkaline Hydrolysis, 100 C (18)

	$\frac{N/3 \text{ H}_2\text{SO}_4}{k^a}$	$\frac{N/10 \text{ NaOH}}{k^b}$
Na methyl α -sulfo palmitate	0.0062	0.14
Na methyl α -sulfo stearate	0.0068	0.10
Na ethyl α -sulfo palmitate	0.0050	0.048
Na butyl α -sulfo palmitate	0.0042	0.028
Na amyl α -sulfo stearate	---	0.053
Na isopropyl α -sulfo palmitate	0.0024	0.006
Na Sec butyl α -sulfo palmitate	0.0025	0.002

^aFirst order reaction: $k = 1/t \ln a/a-x$, in reciprocal min.^bSecond order reaction: $k = \frac{1}{t} \frac{x}{a-x}$ in liters/mole/min.

(b) Ester active value (EAV) = (SV-AV) - UEV.

(c) Theoretical ester value (TEV) based on 100% ester active and molecular weight of product.

(d) % Ester active = $\frac{\text{EAV}}{\text{TEV}} \times 100$.

(e) % NEA = MBA - % ester active.

Other analyses consisted of:

- Total Solids: 1-2 g sample in oven at 110 C for 1 hr.
- % Salt, by difference: Total solids - (active + unsulfonated ester).
- Viscosity: Brookfield.
- Color: 5 wt % solution - Klett - Summerson Colorimeter.
- pH: 1% aqueous solution.

TABLE II

Comparative Saponification of Esters at Two pH Levels

	% Breakdown at 100 C (1 hr)	
	9.7 pH	11.0 pH
Methyl palmitate (R-CH ₂ -C(O)-OCH ₃)	100	100
Na α -sulfo methyl tallow ester (R-CH(CO)OCH ₃) SO ₃ Na	0.2	2.1
Disodium 2-sulfoethyl α -sulfo-palmitate R-CH(CO)O-CH ₂ -CH ₂ -SO ₃ Na	8.3	41.2

of 3-10 at 20, 40, and 60 C. Stirton (38) refluxed 0.01 mole of the ester in 100 ml of 0.1 N NaOH at 100 C and titrated 10-ml samples at selected intervals. He found that the alkaline hydrolysis corresponded to a second order reaction.

Analysis of Sodium α -Sulfo Esters

Because the analytical methods available in the literature (8,16,39) are limited and sketchy, the writers have chosen to outline the various analyses used for a neutralized slurry of a tallow-derived alpha sulfo fatty ester.

- Methylene Blue Active (MBA): The % total active on the monosodium α -sulfo ester and disodium α -sulfo salt was done by the Hyamine method using methylene blue indicator (40,41).
- Unsulfonated Ester Value (UEV): Extraction method using petroleum ether (42). The percentage was converted to the ester value.
- Acid Value (AV): Potentiometric titration, using 0.2 or 0.5 N NaOH (43,44).
- Saponification Value (SV): Potentiometric titration, refluxed 3 hr with 0.5 N NaOH, finally titrated the mixture with 0.2 N or 0.5 N HCl (45).
- Non-ester active (NEA): Calculated as shown below.
 - Total ester value = SV-AV.

TABLE III

Aqueous Solubility

	α -Sulfo acid (%)	Monosodium α -sulfonate (%)	Disodium α -sulfonate (%)	Methyl ester of α -sulfonate (Na Salt) (%)
Lauric	25	.42	4.3	---
Myristic	25	.11	1.5	---
Palmitic	25	.02	0.25	1 @ 29 C
Stearic	13	.01	0.10	1 @ 39 C

PROPERTIES OF SODIUM α -SULFO FATTY ACID ESTERS

Hydrolytic Stability

Stirton et al. (38) found that the sodium salts of alkyl α -sulfo palmitates and α -sulfo stearates were unexpectedly resistant to hydrolysis compared to fatty acid esters. The hydrolysis of α -sulfo fatty acid esters in alkaline medium was a second order reaction and in acid medium, first order. The k values for some sodium α -sulfo fatty esters in acid and alkaline medium are listed in Table I.

Knaggs et al. (46) observed a similar effect with highly purified sodium α -sulfo tallow methyl ester, i.e., the alkaline hydrolysis was faster than acid hydrolysis, but both reactions were very slow.

They also compared the saponification data of ester and sulfoester at two pH levels (Table II) and concluded that esters of α -sulfo fatty acids are substantially more stable than unsulfonated esters due to the stabilizing action of the adjacent sulfo group.

Stein et al. (9,10) have graphically depicted the hydrolytic stability of palm-kernel and coco methyl ester sulfonate by plotting % hydrolysis/hr as a function of temperature and pH at a concentration of 3.4 g of ester sulfonate/liter in aqueous solution, i.e., a concentration which corresponds to concentration in washing solution. They found that at temperatures of up to 60 C the ester hydrolysis was very slow between pH 3-9.5. Mention was made of the stability of a neutral detergent-solution, containing the salt of the α -sulfo fatty ester, over a prolonged period of time. Also there was minimal hydrolysis during spray drying of a detergent slurry containing the α -sulfo compound.

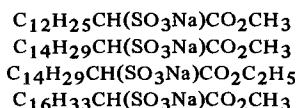
Physical

Aqueous solubility: Table III compares the solubility of the sodium α -sulfo methyl ester of the detergent range fatty

acids with their corresponding α -sulfo acid, mono and disodium salt at 25 C.

As Table III indicates, the α -sulfo acids are easily soluble in water, but the solubility of monosodium salt decreases sharply. Disodium salts formed from the complete neutralization are somewhat more soluble. The blocking of the carboxyl group by esterification results in a more soluble product than the monosodium salt. Stirton et al. (18) have measured the Kraft point, (the temperature at which a 1% aqueous dispersion changes sharply to a clear solution on gradual heating) of various salts of α -sulfo palmitate and stearate. They concluded that most of the Li, NH_4 , and Na salts are too soluble to have measurable Kraft points and form clear 1% solution even at 1 C. The solubility also increased with increase in molecular weight of alcohol, i.e., in going from methyl \rightarrow ethyl \rightarrow propyl.

Lime soap dispersing ability: Stirton and co-workers (7) examined a series of esters of the general formula $\text{RCH}(\text{SO}_3\text{Na})\text{CO}_2\text{R}'$ and concluded that the esters were useful as wetting or lime soap dispersing agents depending on their structure and chain length. Esters which showed lime soap dispersing characteristics had an unsymmetrical structure with the hydrophilic portion at or near the end of the molecule. For example:



The lime soap dispersing ability of the α -sulfo sodium methyl esters of detergent range fatty acids compared to sodium alkylbenzene sulfonate as measured by the method of Borghetty and Bergman (47) are shown in Table IV.

Calcium stability: The esters are more resistant to precipitation by metal ions than the corresponding sodium α -sulfo myristic, α -sulfo palmitic, or α -sulfo stearic acid. Table V gives the calcium stability for some of the esters of α -sulfo palmitate and stearate according to Stirton et al. (28).

Biological Properties

Stein et al. (9) have stated that both the α -sulfo ester sulfonates and the α -sulfo acid were easily biodegraded,

TABLE IV

Lime Soap Dispersing Ability of Various Lime Soap Dispersing Agents

Lime soap dispersing agent	Borghetty-Bergman Value ^a
Sodium α -sulfo methyl myristate	9
Sodium α -sulfo methyl palmitate	9
Sodium α -sulfo methyl stearate	9
Sodium α -sulfo methyl tallowate	8
Sodium α -sulfo ethyl tallowate	10
Sodium linear alkylbenzene sulfonate (LAS)	40

^aThe number of grams of lime soap dispersing agent which have to be added to 100 g of sodium oleate just to prevent the formation of a lime soap curd in hard water. A low value corresponds to high lime soap dispersing ability.

TABLE V

Calcium Ion Stability^a

$\text{RCH}(\text{SO}_3\text{Na})\text{CO}_2\text{R}'$	Calcium stability (ppm CaCO_3)
Sodium α -sulfo methyl palmitate	1800
Sodium α -sulfo ethyl palmitate	1800
Sodium α -sulfo methyl stearate	800
Sodium α -sulfo ethyl stearate	540
Sodium α -sulfo methyl myristate	1800
Sodium α -sulfo ethyl myristate	1800

^aExcellent stability of these esters to Mg, Fe, Ni, Cu, and Zn were reported by the authors.

possessed low acute oral toxicity, and had good skin compatibility. Weil et al. (48,56) had studied the biological properties of several esters and their conclusions were similar to those found by Stein. The biological properties of fatty methyl ester sulfonates are shown in Table VI below.

Recently, Linfield et al. (49) compared the biodegradability of sodium methyl α -sulfo tallowate (TMS) with linear alkylbenzene sulfonate (LAS) by the Presumptive Soap and Detergent Association method and obtained the following results:

TABLE VI

Biological Properties of the Na Salts of α -Sulfo Methyl Esters of Fatty Acids

	Biodegradability 80-100% ^a	Acute oral toxicity ^b LD ₅₀ (g/kg body wt)	Skin Irritation ^c
Sodium α -sulfo methyl myristate	3 days	3	N.R.
Sodium α -sulfo methyl palmitate	4.3 days	3	N.R.
Sodium α -sulfo methyl stearate	3.9 days	3	N.R.
Sodium α -sulfo methyl tallowate	4 days	2.7	N.R.
Sodium lauryl sulfate	3 days	---	---
Sodium lauryl ether sulfate	6 days	---	---
Sodium linear alkylbenzene sulfonate	24 days	---	---

^aRiver Water Die Away test.

^bRat feeding experiments. Single dose or when necessary, closely spaced multiple doses of an aqueous solution via stomach tube.

^cA 2% solution applied to shaved back of albino rats.

TABLE VII

Surface and Interfacial Tension 0.2%, 25 C

	dynes/cm	
	S.T.	I.T.
Sodium methyl α -sulfo myristate	39.9	10.9
Sodium methyl α -sulfo palmitate	39.0	9.7
Sodium methyl α -sulfo stearate	39.0	8.4
Sodium ethyl α -sulfo myristate	39.6	10.1
Sodium ethyl α -sulfo palmitate	36.4	8.0

TABLE VIII

Surface Tension, Salts of Alkyl Esters of α -Sulfo Stearic Acid, 0.1% Solution, 25 C, $C_{16}H_{33}CH(SO_3M)CO_2R'$

R'	Li	Na	K
CH ₃	42.2	39.7	a
C ₂ H ₅	41.0	38.7	a
C ₃ H ₇	40.0	37.6	35.6
(CH ₃) ₂ CH	40.1	37.9	35.8
C ₄ H ₉	38.8	36.4	33.4

^aInsufficiently soluble.

TABLE IX

Foaming Properties

0.25% Solution, 60 C	Distilled water	300 ppm
	mm	mm
Na methyl α -sulfo palmitate	210	225
Na ethyl α -sulfo palmitate	210	215
Na butyl α -sulfo laurate	220	230
Na amyl α -sulfo laurate	220	235
Na dodecyl α -sulfo butyrate	200	225
Na tetradecyl α -sulfo propionate	220	240

	% Degradation After 7 days
TMS	100
LAS	92

Other Surface Active Properties

Besides lime soap dispersing ability (LSDA), Stirton (16) examined other properties of the Na salt of α -sulfo fatty acid esters, which are most directly related to their use as surface active agent or detergent.

TABLE XI

Launder-O-meter Cotton Detergency Test

Detergent 0.25% solution, 60 C	Detergency, ΔR^a	
	0 ppm	300 ppm
Na methyl α -sulfo myristate	32	16
Na methyl α -sulfo palmitate	31	21
Na methyl α -sulfo stearate	31	21
Na dodecyl sulfate	28	24
Na octadecyl sulfate	38	32

^a ΔR = increase in reflectance after washing standard soiled cotton.

Surface (S.T.) and Interfacial Tension (I.T.) (28)

The S.T. and I.T. of esters of some Na α -sulfo fatty acids were measured at 0.2% solution in distilled water at 25 C with the du Nouy tensiometer. The data are assembled in Table VII.

Stirton et al. (18) further observed that in the α -sulfo fatty esters the surface tension decreases or increases with the change of the cation as shown in the table below for Li, Na, and K salts of alkyl esters of α -sulfo stearic acid (Table VIII).

Foaming Properties

According to Stirton (28), esters with 17-20 C atoms have the best foaming properties where the foam remains stable for 5 min (Table IX).

Knaggs' paper (46) gives data on Ross Miles foam heights for 0.1% active detergent range α -sulfo fatty esters in water ranging from 0 to 1000 ppm hardness. The data are shown in Table X and are compared with some commercially available surfactants.

Inspection of these data reveals that the Na and triethanolamine salts of α -sulfo methyl tallowate (C_{16} - C_{18}) are moderate foamers, whereas the salts of α -sulfo methyl myristate (C_{14}) are high foamers and remain moderate foamers over the entire range of water hardness (0-1000 ppm). Knaggs further mentions that the Ross Miles Foam data at 0.05% and 0.01% actives concentration also shows the α -sulfomyristic esters to be much more effective than most conventional surfactants.

Detergency

Stirton (28) has shown that α -sulfo fatty acid esters containing 17-19 carbon atoms with the hydrophilic group near the end of the molecule had the best detergency. Table XI gives the increase in reflectance (ΔR) values in soft and hard water after washing ten swatches of standard soiled cotton (G.D.C. No. 26) with 0.25% solution in a Launder-O-meter at 60 C. The data obtained are compared

TABLE X

Ross Miles Foam Heights

0.1% Active solution, 25 C	Initial foam, mm				
	0	35	140	350	1000
	ppm	ppm	ppm	ppm	ppm
Na α -sulfo methyl myristate	159	175	180	175	159
Na α -sulfo methyl laurate	150	172	171	155	152
Na α -sulfo methyl tallowate (C_{16} - C_{18})	137	135	80	48	30
TEA α -sulfo methyl tallowate	135	234	90	62	26
TEA α -sulfo methyl myristate	150	172	171	155	152
NH ₄ α -sulfo methyl myristate	170	180	175	180	170
Sodium alkylbenzene sulfonate	179	179	178	144	112
Sodium lauryl sulfate	186	76	81	74	30
Sodium lauryl ether sulfate	183	180	175	175	154

with sodium dodecyl sulfate and sodium octadecyl sulfate as reference standards.

USES AND APPLICATION OF α -SULFO FATTY ACID ESTERS

Initial use suggestion for the α -sulfo esters was for textile applications (50). In recent times they have received attention as components for detergent powder (51,52) and liquid compositions (53,54) as well as soap-detergent bars (55). The methyl esters of α -sulfonated hydrogenated tallow fatty acids, being good lime soap dispersing agents, have been formulated with soap and builders to give an effective detergent for hard water laundry use (49). They have also been suggested for use as ore flotation agents (57). Stein (10) has mentioned that special esters of α -sulfo fatty acids can also be used as mold release agents for rubber and polyurethane elastomers and have been recommended to be used in formulating spin finish agents used with synthetic fibers. Salts of α -sulfonated fatty esters can be used in cosmetic preparation as surfactants in toothpastes and shampoos.

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