Alpha Olefin Sulfonates from a Commercial SO$_3$-Air Reactor[1]

D. M. MARQUIS, S. H. SHARMAN, R. HOUSE and W. A. SWEENEY,
Chevron Research Company, Richmond, California

Abstract

Alpha olefin sulfonate (AOS) can be made by SO$_3$-air sulfonation of straight chain alpha olefins followed by saponification of the neutralized product. The sulfonation step forms unsaturated sulfonic acids, sultones and sultone sulfonic acids. Hydrolysis of the various sultones yields a mixture of unsaturated and hydroxy sulfonates. Sulfonation of commercial mixtures of straight chain alpha olefins in a large-scale SO$_3$ falling film unit has given AOS of 1.5–3.0% oil based on active content and tristimulus color of about 40% saturation (2% solution) which is readily bleachable with 1–3% NaOCl to about 10–15% saturation.

Performance of AOS made from C$_{15}$–C$_{18}$ alpha olefin is comparable to that of the high-foaming C$_{11}$–C$_{14}$ LAS in both detergency and dishwashing foam. It is superior to similar products made from internal straight chain olefins. The product shows a low order of toxicity and biodegradability slightly better than that of LAS. A C$_{15}$–C$_{16}$ AOS blend is especially attractive in liquid detergent formulations.

Introduction

THE DEVELOPMENT of a commercially feasible process for the preparation of surfactants by direct reaction of SO$_3$ with alpha olefins and the properties of the products made by such a process form the subject of this paper.

Our initial work was performed in a laboratory batch reactor with conditions confined to the use of vaporized SO$_3$ diluted with air in the absence of solvent. In contrast to the situation with long chain alkylbenzenes, under these conditions it is necessary to use a rather large excess of SO$_3$ to obtain high olefin conversion and, due to the vigorous reactivity of SO$_3$, dark products are obtained. The extent of this problem is illustrated in Figure 1.

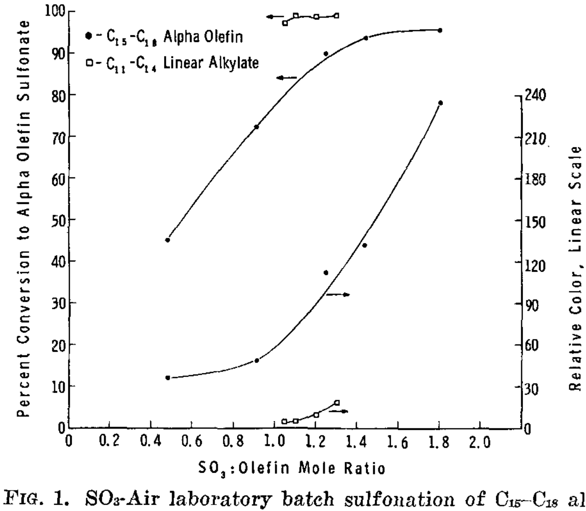
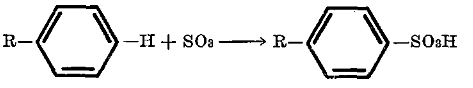


FIG. 1. SO$_3$-Air laboratory batch sulfonation of C$_{15}$–C$_{18}$ alpha olefins.

In view of the need for such a large excess of SO$_3$ in a laboratory batch reactor, isomerization of olefin, and formation of small amounts of both the very insoluble 2-hydroxy sulfonate and dimeric sultone, we turned our attention to products made in a continuous reactor. As anticipated, the short reaction time attainable in a continuous, falling film reactor eliminated most of these problems.

Chemical Background

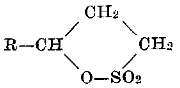
The reaction of alpha olefins with SO$_3$ differs from that of alkylbenzenes in one important respect: a saponification step is required in order to convert the neutral products initially formed into sulfonates. This is not a simple hydrolysis of sulfonic anhydrides as in the case of alkylbenzenes (1). The reaction of alkylbenzenes results in the overall change of inserting the SO$_3$ *into* a C—H bond (Equation 1).

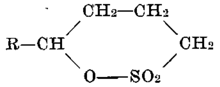

[1]

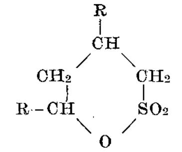
With alpha olefins, two reaction paths account for the major products. Direct insertion of SO$_3$ results in formation of alkene sulfonic acid with concomitant migration of the double bond (Equation 2) (2,3).

$$R{-}CH{=}CH_2 + SO_3 \rightarrow R'{-}CH{=}CH{-}(CH_2)_x{-}SO_3H \qquad [2]$$

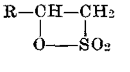
Sultones are formed by the second path. Sultones which have been identified are 1,3 (I), 1,4 (II), and dimeric 1,4 (III), analogous to those isolated by Bordwell in his pioneering work on SO$_3$-olefin reactions (4–6). More recently, a series of 1,3-sultones has been unambiguously synthesized from detergent range alpha olefins (3).

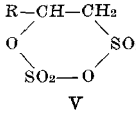

I


II


III

Saponification converts these sultones to a mixture of the corresponding alkene sulfonates and hydroxy alkane sulfonates. The final product from batch reaction also contains 2-hydroxy sulfonate, a very insoluble material. The origin of this product may be either 1,2-sultone (7) (IV) or carbyl sulfate (8) (V).

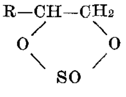

IV


V

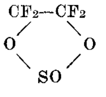
The remaining neutral material which is isolated by petroleum ether extraction from aqueous ethanol solution consists mainly of paraffin (starting olefin contains about 1% paraffin) and internal olefin. No evidence has been found for a cyclic sulfite (VI), analogous to the one reported from tetrafluoroethylene (VII) (9). However, the presence of less than 0.2% of sulfur-containing material, believed to be a cyclic sulfate (VIII), has been inferred from mass spectrometric analysis.

---

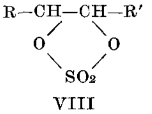
[1] Presented at the AOCS Meeting, Los Angeles, April 1966.



VI



VII



VIII

Many of the compounds mentioned in this section appear to result from the necessarily long reaction time of a batch run and the presence of local excesses of SO_3 or olefin in the reaction medium. The formation of these undesirable by-products from batch reactions formed part of the incentive for working in a continuous reactor, a change which did in fact eliminate them.

Semicommercial Scale Continuous Sulfonation of Single-Carbon Olefins

Preparation and Properties

Using Allied Chemical Company's semicommercial SO_3 reactor, we have sulfonated a number of olefins to study the chemistry involved and also the performance of the derived products which we have called alpha olefin sulfonate (AOS). From our laboratory batch studies, we knew that both dishwashing foam and detergency reached a maximum in the range C_{16} to C_{17}. Accordingly, all of the olefins from C_{14} through C_{19} were sulfonated individually. There are slight product variations because the individual olefins were obtained from different sources and there were slight differences in process conditions. Nonetheless, the results clearly showed that with this semicommercial unit high conversions can be obtained using only a 10–15 mole percent excess SO_3. Extractable oils in the range of 1–3% based on active content were obtained.

Using 1-hexadecene as the model olefin for limited chemical studies, we found by hydrogenation that the final saponified product consisted of about 53% alkene sulfonate and 47% hydroxy sulfonate. The hydroxy sulfonate is believed to be mainly 3-hydroxy sulfonate, derived from the 1,3-sultone. No 2-hydroxy sulfonate was found, in contrast to the product from the laboratory batch reactor.

Using the oxidation procedure of von Rudloff (10), which has been shown to be valid for an authentic $\Delta^{2,3}$ alkene sulfonate (11), the double bond in the alkene sulfonate portion was found to be mainly in the 2,3 and 3,4 positions. However, the double bond migration extended as far down the chain as the 11,12 position in contrast to the results reported by Püschel and Kaiser who used different batch sulfonation conditions (11). The distribution of unsaturation is shown in Table I. The extent to which the product is derived from internal olefin formed by isomerization has not been determined.

The amount of disulfonic acid and sultone-sulfonic acid was determined by quantitative, room temperature neutralization followed by separate saponification of the oil and aqueous phases. In a sulfonation which employed a 1.24 SO_3:olefin mole ratio, we found 23% alkene sulfonic acid, 7% disulfonic acid, 18% sultone-sulfonic acid, and 52% sultone by weight. This analysis, plus the inorganic sulfate found (about 3%) accounts well for all the SO_3 used. These calculations were made assuming no trifunctional compounds were present.

Difunctional compounds are probably formed by attack of SO_3 on the double bond of the initially formed alkene sulfonic acid (Equation 2). Another possibility is that difunctional compounds are formed by direct attack of SO_3 on the paraffin side chains. It is unlikely that this will occur when double bonds are available for reaction, even though we have shown in separate experiments that SO_3 will react with paraffin hydrocarbons under olefin sulfonation conditions.

TABLE I
Sulfonation of 1-Hexadecene with SO_3-Air in a Continuous Falling Film Reactor

Mole ratio SO_3: AO		1.15
Oil, based on active, %		0.75
Composition of product, after saponification		
Alkene sulfonates, % [a]		53
Hydroxy sulfonates, % [a]		47
$RCH{=}CH{-}(CH_2)_xSO_3Na$		
x	*Mole %*	
0	9	
1	21	
2	16	
3	5	
4	6	
5	6	
6	7	
7	6	
8	7	
9	8	
10	9	

[a] Includes disulfonates.

When internal olefins are substituted for alpha olefins, a much greater excess of SO_3 must be used to get complete conversion. This indicates that much more of the olefin forms difunctional products.

Performance

The single carbon AOS samples made in the continuous reactor were used to evaluate the effect of molecular weight on detergency and dishwashing foam performance. The results confirmed that C_{14} through C_{19} is indeed the proper molecular weight range for study. Detergency relative to a pair of standards was measured in the Terg-O-Tometer with Foster D. Snell soil. A 25% active heavy-duty solid formulation was chosen for this screening test.

As can be seen (Fig. 2), in soft water the C_{16}, C_{17}, C_{18}, and C_{19} AOS materials perform well through the concentration range studied. The C_{14} sulfonate, on the other hand, is quite poor, while the C_{15} sample is intermediate, being an inadequate performer at low concentration. In hard water all but the C_{14} surfactant perform well.

The single-carbon samples were also studied in a hand dishwashing foam test using shortening soil. The results are depicted in Figure 3. In the 25% active heavy-duty formulation, they show clearly, in spite of some fluctuations, that the C_{15}, C_{16}, C_{17}, and C_{18} sulfonates are excellent performers in both hard and soft water. The C_{14} and C_{19} species fall off badly. The hexadecyl AOS seems to be the optimum performer. Performance of a high foaming C_{11}–C_{14} LAS (sulfonate of Oronite Alkane 1060) is shown for comparison.

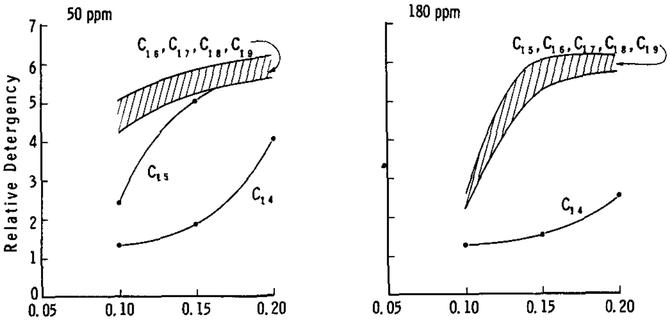


FIG. 2. Detergency of single carbon AOS. Heavy-duty formulation (25/0) FDS soil.

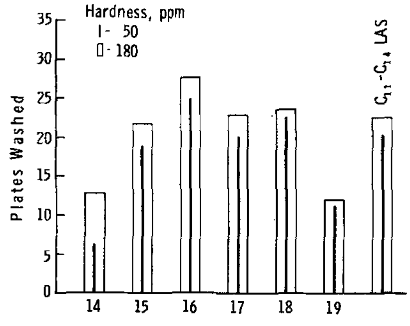


FIG. 3. Dishwashing foam of single carbon AOS. Heavy-duty formulation (25/0).

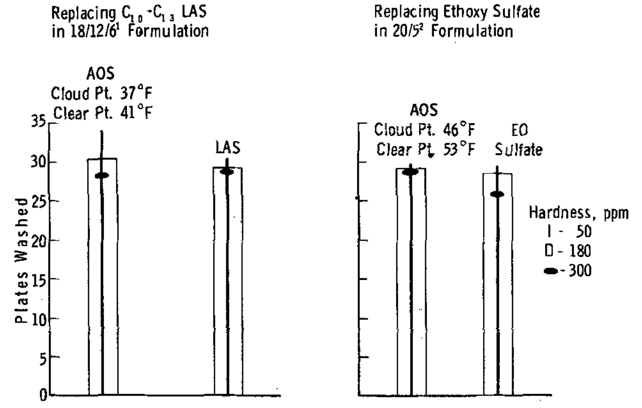
Two light-duty liquid formulations were studied. One contained, in addition to the test surfactant, a C_{12}–C_{15} primary alcohol ethoxamer sulfate plus an alkanolamide foam booster, the other an amine oxide. These data are shown in Figure 4. Performance of single-carbon AOS in the first formulation is compared with that of a C_{10}–C_{13} LAS (sulfonate of Oronite Alkane 1056) and in the second with a lauryl ethoxamer sulfate. As in the heavy-duty formulation, the C_{15}, C_{16}, C_{17}, and C_{18} sulfonates perform very well. In addition, performance of the low molecular weight members of the range does not fall off as much as it does in the heavy-duty formulation.

These data encouraged us to test a 1/1 blend of the C_{15} and C_{16} sulfonates. The results, depicted in Figure 5, show that performance in the light-duty liquid formulations is excellent. In addition, the blend displays very high solubility; for example, the 18/12/6 formulation has cloud and clear points at 37F and 41F, respectively, which conform with usual commercial requirements.

Semicommercial Scale Continuous Sulfonation of C_{15}-C_{18} Olefin

Preparation and Properties

With the same semicommercial equipment, a broader range alpha olefin (Chevron C_{15}–C_{18}) was also converted to AOS. Using 16% excess SO_3, the product had an average equivalent weight of 343 and a sulfonate-to-salt ratio of 97:3. As with the single-carbon olefins, continuous processing resulted in sulfonate products with low oil and acceptable color. Oil contents between 1.8% and 2.6% based on active and a color of 44% saturation (tristimulus, 2% solution) or about 700 Klett are typical. The material can be bleached readily with 0.5–3% sodium hypochlorite resulting in color values of 7–23% saturation (115–350 Klett) which are fully in the range of commercial surfactants. Figure 6 shows the results of bleaching experiments performed in the laboratory. Also shown is a point for bleaching in a pilot plant using 3% sodium hypochlorite. This product had a color value of 7% saturation and has shown no tendency to color reversion or rancidification. It shows dishwashing foamability equal to that of the unbleached material. We expect that further refinement of process conditions will lead to even lower colors and oils.

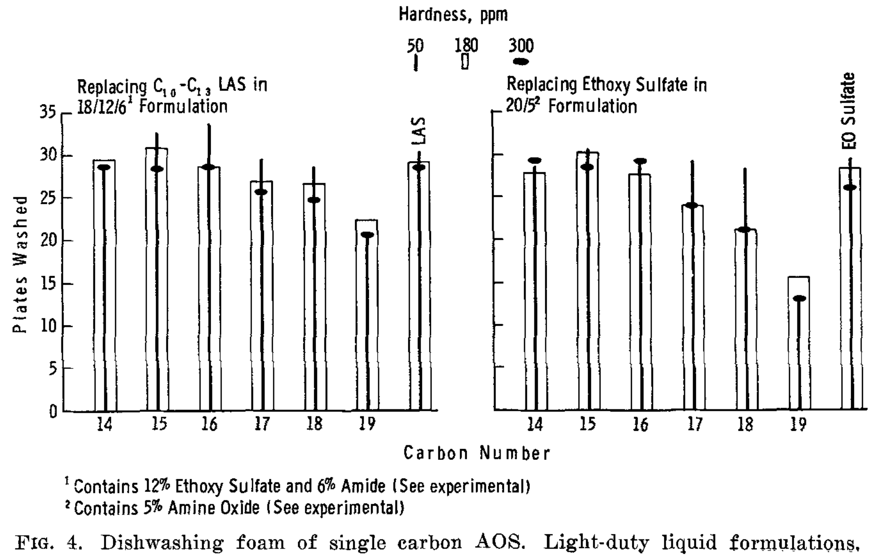


[1] Contains 12% Ethoxy Sulfate and 6% Amide (See experimental)

[2] Contains 5% Amine Oxide (See experimental)

FIG. 5. Dishwashing foam of C_{15}-C_{16} blend. Light-duty liquid formulations.

The C_{15}–C_{18} AOS is a highly soluble surfactant as shown by cloud points in Figure 7. Trace quantities of slowly redissolvable materials give a high clear point. The high solubility is especially well demonstrated by the fact that the cloud point curve for the AOS is well below those of the C_{10}–C_{13} and C_{11}–C_{14} LAS. Figure 8 shows that the substance possesses a high degree of stability under oxidation conditions. In an elevated temperature accelerated oxidation test, it becomes rancid much more slowly than



[1] Contains 12% Ethoxy Sulfate and 6% Amide (See experimental)

[2] Contains 5% Amine Oxide (See experimental)

FIG. 4. Dishwashing foam of single carbon AOS. Light-duty liquid formulations.

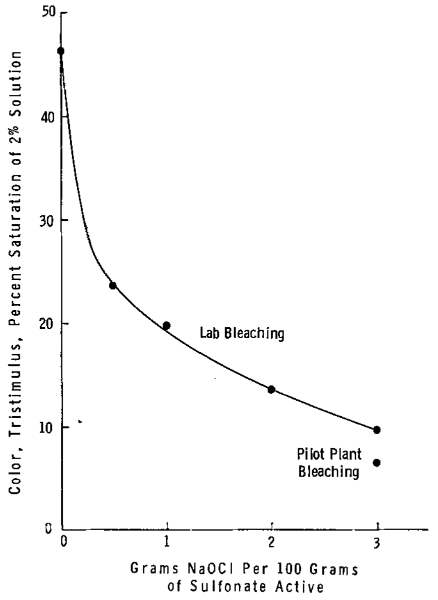


FIG. 6. Effect of bleach on color of C_{15}–C_{18} AOS.

	Surfactant Odor		
Time at 70°C, Days	Tallow Alcohol Sulfate	C_{15}-C_{18} AOS	C_{10}-C_{13} or C_{11}-C_{14} LAS
0	Mild	Odorless	Odorless
1	Mild	Trace	Trace
2	Moderate*	Slight**	Very Slight
3	Moderate*	Slight**	Very Slight
7	Moderate (Sl. Rancid)	Slight**	Slight**
10	Moderate (Sl. Rancid)	Slight**	Slight**
14	Fairly Strong (Sl. Rancid)	Mild**	Rancid
17	Fairly Strong (Sl. Rancid)	Mild**	Very Rancid
18	Fairly Strong (Sl. Rancid)	Moderate (Trace Rancid)	Very Rancid
21	Fairly Strong (Sl. Rancid)	Fairly Strong (Sl. Rancid)	Very Rancid

Odor Scale

Odorless
Trace
Slight
Mild
Moderate
Strong

Increasing Odor ↓

*Butter-like odor, not rancid.
**Characteristic odor, not rancid.

FIG. 8. Storage stability. Accelerated test (70C) on dried surfactants.

does LAS. It shows no tendency toward decomposition on drum drying, giving a nontacky, free flowing powder; thus, spray drying should present no problem.

The C_{15}–C_{18} AOS is highly biodegradable as would be expected of a straight chain structure. As shown in Figure 9 for both a river die-away type test and the shake culture test employed by the Soap and Detergent Association (12), it is more degradable than LAS. The substance gives a fairly typical surface tension lowering versus concentration curve (see Fig. 10).

Human skin irritation was negligible as measured by patch tests using panels of ten individuals and surfactant concentrations of 1% and 2%. The C_{15}–C_{18} AOS produced no irritation under conditions in which LAS caused a slight reaction. Oral toxicity was also extremely low. Measured on mice, the LD_{50} was 2.5 g surfactant/kilogram body weight for both bleached (3% sodium hypochlorite bleach) and unbleached material. This represents toxicity slightly less than that of LAS.

Performance

The C_{15}–C_{18} AOS was found to be generally similar in performance to the high foaming-type C_{11}–C_{14} LAS. A variety of heavy-duty solid and light-duty liquid formulations was used in the same tests employed for the single-carbon materials, plus a detergency test using natural soil and a detergency-foaming test using a front loading washing machine. These results are shown in Figures 11 through 19. Terg-O-Tometer detergency using FDS soil is higher than would be predicted from the single-carbon data. This difference is within experimental error.

A sulfonate made from C_{15}–C_{18} internal olefin was found to be deficient in foamability. Sulfonation with a 1.35:1 ratio of SO_3:olefin yielded a high oil sulfonate (8%) which, after deoiling, gave a dishwashing foam value of only 6 plates in a 25/0 formula.

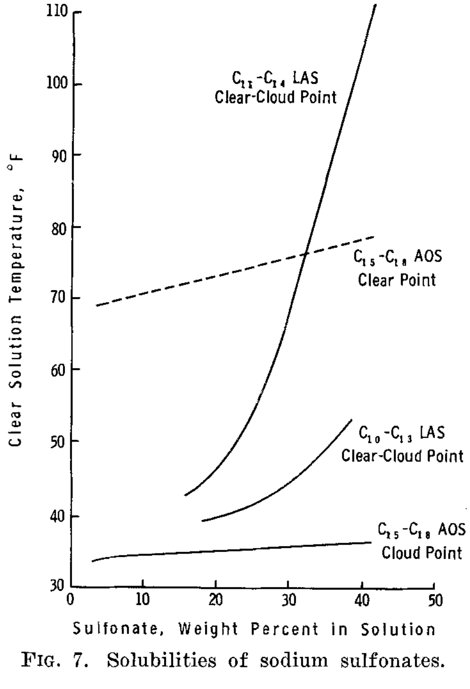
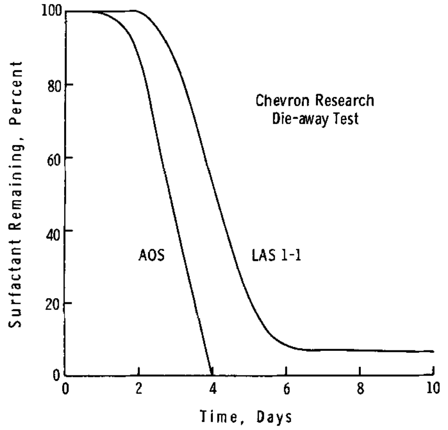


FIG. 7. Solubilities of sodium sulfonates.



Soap and Detergent Association
Shake Culture Test

Surfactant	Removal, Percent
C_{15}-C_{18} AOS	96-97
LAS 1-1 Standard	90-91*

*Soap and Detergent Association average 93.6

FIG. 9. Biodegradability.

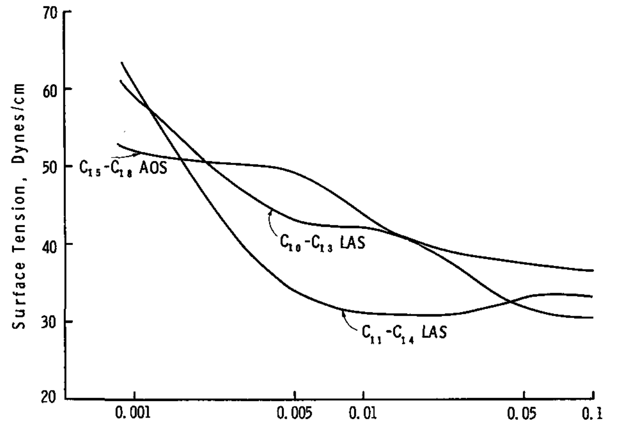


FIG. 10. Surface tension. Surfactant (100% active) in distilled water.

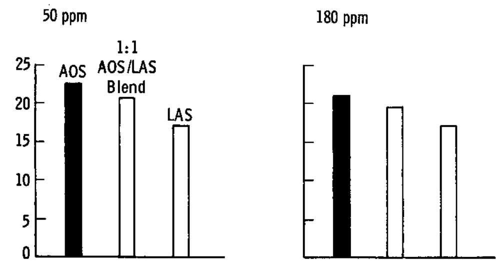


FIG. 12. Dishwashing foam of C_{15}–C_{18} AOS versus C_{10}–C_{18} AOS versus C_{10}–C_{13} LAS. Heavy-duty alkyl sulfate formulation (7.5/9.5).

Experimental

Laboratory Batch Sulfonations

The reactor used consisted of a 300-ml jacketed reactor equipped with a stirrer, baffles, and three 1-mm inside diameter inlets for the air-SO_3 mixture. The gas inlets were equally spaced about the base of the reactor, similar to the reactor previously reported from this laboratory (13).

In a typical run, olefin was charged to the reactor and over a period of about 30 min liquid SO_3 (Sulfan) was fed in vaporized form as a 5% by weight mixture in air. Cooling water in the jacket maintained the temperature in the range of 23C to 50C. The sulfonation product was then poured into aqueous NaOH solution with vigorous stirring. The sultones present were then hydrolyzed by heating the mixture at 90–100C for 2–3 hr. Results with representative olefins are shown in Table II.

The difficulty of attaining high yields in a batch system is illustrated by the material balance shown in Table III where a 29% excess of SO_3 gave only 93% conversion to surfactant, even though 105% of the theoretical SO_3 was incorporated in the organic molecules.

Hexadecane-1,3-Sultone

From a 1-hexadecene sulfonation product which had been cold neutralized with NaOH, the 1,3-sultone was readily isolated by extraction with *n*-pentane, mp 69C, lit. 70–71C (11). The infrared spectrum showed bands at 7.38, 8.42, and 8.66 μ.

Hexadecane-1,4-Sultone

The neutral oil (4.32 g) from reaction of 0.15 mole of 1-hexadecene and 0.144 mole of SO_3 was found by VPC analysis, using an internal standard, to contain 3.92 g of hexadecenes. The infrared spectrum

TABLE II

Laboratory Batch Sulfonations

Olefin used	C_{16}	C_{15}–C_{18}	Isomerized C_{15}–C_{18}	C_{15}–C_{20}	Isomerized C_{15}–C_{20}
mM SO_3 Fed	192	360	216	192	288
mM Olefin	150	250	150	150	200
SO_3: Olefin ratio	1.28	1.44	1.44	1.28	1.44
meq NaOH, total	165	338	173	173	246
meq Active[a]	135	229			157
% Yield active	90.0	91.6			73.6
% Oil, based on olefin charged[b]	9.2	9.3	34.9	12.0	22.3
Olefin accounted for	99.2	100.9			95.9

[a] By Hyamine titration.
[b] By petroleum ether (30–60C) extraction.

TABLE III

Material Balances for SO_3 Sulfonation of 1-Hexadecene

Olefin Balance, mMoles		
Olefin charge		149
Product (hyamine titration)	139	
Internal olefin in oil (VPC)	7.7	
Other oil (nonvolatile in VPC)	2.3	
Total olefin accounted for		149
SO_3 Balance		
SO_3 Fed		192.5
SO_3 in product (by NaOH consumption)	156.1	
SO_3 in tail gas	6.0	
$SO_3 \rightarrow SO_2$	8.4	
$SO_3 \rightarrow Na_2SO_4$	9.2	
SO_3 in oil	1.2	
SO_3 accounted for		180.9

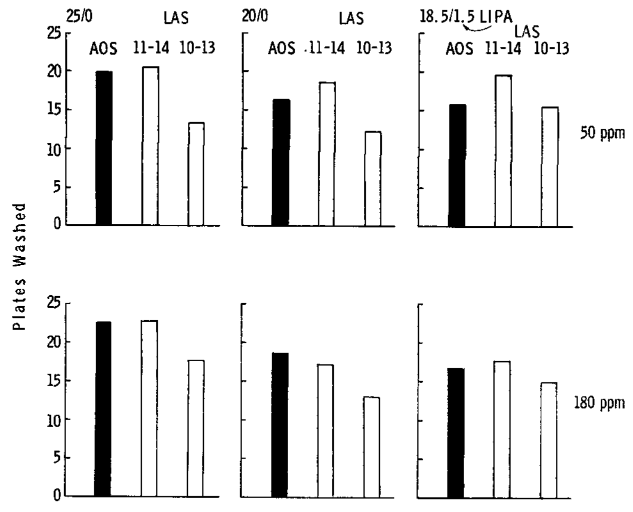
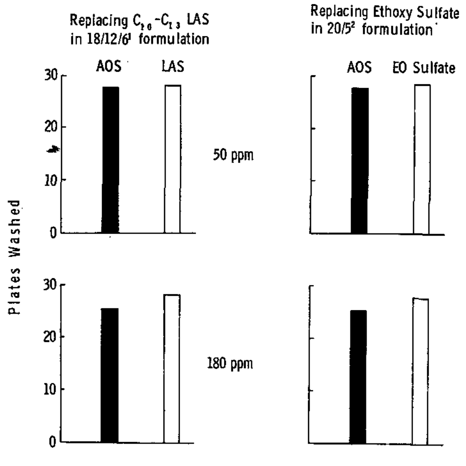


FIG. 11. Dishwashing foam of C_{15}–C_{18} AOS versus LAS heavy-duty formulations.



[1] Contains 12% Ethoxy Sulfate and 6% Amide (See experimental)
[2] Contains 5% Amide Oxide (See experimental)

FIG. 13. Dishwashing foam of C_{15}–C_{18} AOS. Light-duty liquid formulations.

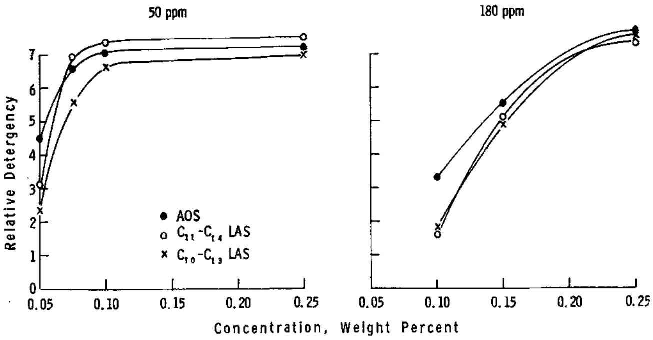


FIG. 14. C_{15}–C_{18} detergency using natural soil. Heavy-duty formulation (25/0).

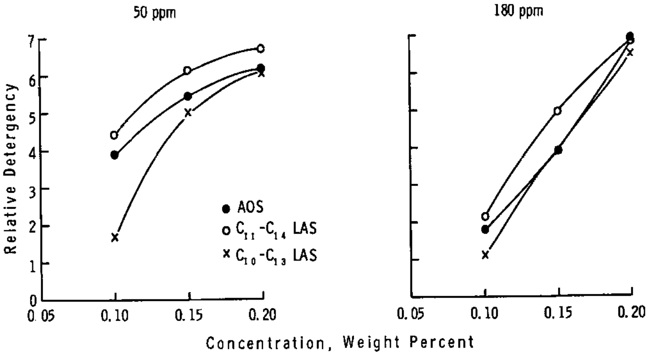


FIG. 16. C_{15}–C_{18} AOS detergency using FDS soil. Heavy-duty formulation (20/0).

of the oil showed an olefin band only at 10.3 μ, indicating trans-internal olefin. On standing, the oil partly solidified. The liquid portion was removed by suction filtration, and the remaining solid was washed with cold pentane. The product, clearly still somewhat impure, weighed 80 mg, and had a melting range of 52–55C. The infrared spectrum of this material shows a strong absorption at 11.15 μ, which is absent from the spectrum of the 1,3-sultone. (1,4-Butane sultone shows a strong band at 10.92 μ.) There is also a single peak at 8.55 μ rather than the doublet at 8.42, 8.66 μ for the 1,3-sultone. The NMR spectrum shows less resolved, broad peaks in the same regions as for the 1,3-sultone. From integration of the peak areas, the CH_2:CH_3 ratio is approximately 13:1, ruling out a sultone derived from internal olefin. The analysis shown below, though not in precise agreement with that calculated for $C_{16}H_{32}SO_3$, probably because of the impurity of the sample, nevertheless provides some additional support for the assignment of structure.

Analysis for $C_{16}H_{32}SO_3$:

Calculated—C, 63.16; H, 10.53; S, 10.53
Found —C, 63.75; H, 10.52; S, 8.96
63.80 10.81

The apparent low yield of sultone actually isolated was due to its high solubility in *n*-pentane. The amount was 1.2% assuming all of the nonolefin portion of the oil (0.40 g) was sultone.

Dodecylene Glycol Sulfite

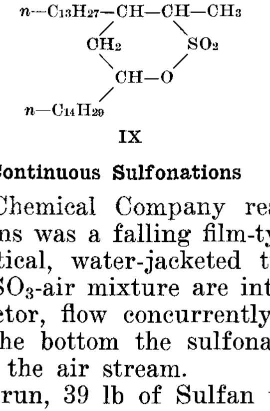
As a model compound, dodecylene glycol sulfite was prepared by reaction of dodecane-1,2-diol with thionyl chloride. The infrared spectrum of the product showed the same bands as 1,2-propylene glycol sulfite (Aldrich Chemical): 6.85 μ (s), 7.30, 7.52 (m), 8.30 (v.s.), and 10.42 μ (broad). None of these bands was observed in the neutral oil described in the preceding section.

Hexadecane Dimer Sultone

The oil isolated from the material balance run (see above) also partly solidified on standing. The solid portion, amounting to less than 1%, showed a band at 11.15 μ in the infrared, indicating 1,4-sultone. Mass spectrometric analysis showed the following ions:

m/e	*Assignment*
514	$C_{31}H_{61}SO_3+$
498	$C_{30}H_{59}SO_3+$
484	$C_{29}H_{57}SO_3+$
446	$C_{32}H_{64}+$
420	$C_{30}H_{60}+$
291	$C_{15}H_{30}SO_3+$

This cracking pattern is consistent with the structure IX.



IX

Semicommercial Continuous Sulfonations

The Allied Chemical Company reactor used for these sulfonations was a falling film-type unit in the form of a vertical, water-jacketed tube. Both the olefin and the SO_3-air mixture are introduced at the top of the reactor, flow concurrently down the reactor, and at the bottom the sulfonated product is separated from the air stream.

In a typical run, 39 lb of Sulfan was introduced in the course of one hour in an air stream of 85 standard cubic feet per minute; and simultaneously 95.5 lb of C_{15}–C_{18} alpha olefin whose composition is given in Table IV was fed during the same period.

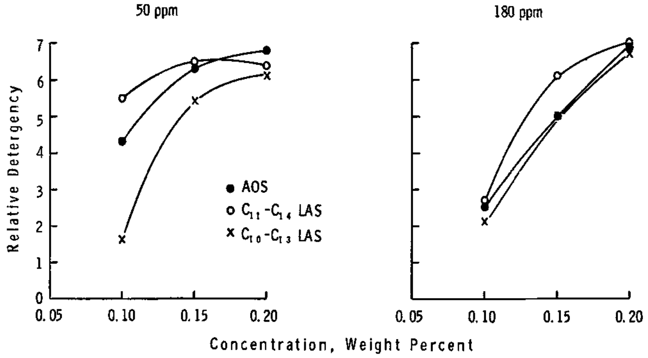


FIG. 15. C_{15}–C_{18} AOS detergency using FDS soil. Heavy-duty formulation (25/0).

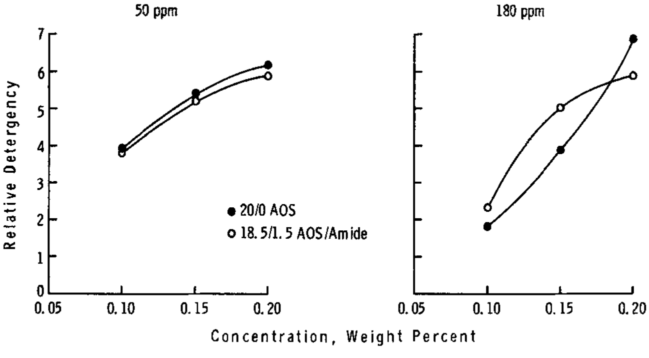


FIG. 17. C_{15}–C_{18} AOS detergency using FDS soil. Heavy-duty formulations showing effect of amide foam booster.

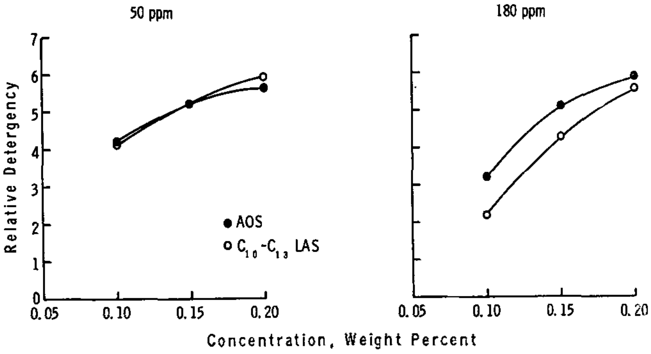


FIG. 18. C_{15}–C_{18} AOS detergency using FDS soil. Heavy-duty alkyl sulfate formulation (7.5/9.5).

Cooling water was applied to the jacket, the temperature of the SO_3-air stream was about 43C, and the product temperature was about 46C. The sulfonated product was neutralized and hydrolyzed by a procedure similar to that described for laboratory batch reactions.

Oxidation of C_{16} AOS

The procedure used to determine the positions of the double bonds in the alkene sulfonate portion of the product was that of von Rudloff (10). A control experiment with pelargonic acid showed there was no further degradation of the initially formed carboxylic acid under the conditions used.

Hydrogenation of C_{16} AOS

Hydrogenation in aqueous solution using 3% of 5% palladium-on-charcoal catalyst proceeded smoothly at 45C and 3 to 4 atmospheres H_2 with the uptake of 53% of the theoretical amount of hydrogen. Since comparative NMR spectra showed all of the unsaturation was removed on hydrogenation, the other 47% is attributed to hydroxy sulfonates.

AOS Properties

The average equivalent weight of the C_{15}–C_{18} AOS was determined to be 343 by titration with the quaternary Hyamine 1622 (diisobutyl phenoxyethoxyethyl dimethylbenzyl ammonium chloride). A sample, deoiled and partially desalted, was plate dried at about 130C and powdered. It was then heated overnight in a vacuum oven at 124 mm pressure and 120C. (Other experiments in which the powder had been vacuum dried overnight at 110C and 140C, respectively, resulted in identical equivalent weights.) Carefully weighed samples of the resulting dry powder were then dissolved in distilled water, and Hyamine titrations were performed. The powder was assumed to be 97% detergent active since the Na_2SO_4 content had been shown to be 3%.

TABLE IV
Inspections of Chevron C_{15}–C_{18} Alpha Olefin Used in Typical Run

Total olefins, weight percent	98
Straight chain alpha olefins	89
Branched and naphthenic olefins	7
Diolefins	2
Paraffins	2
Carbon number distribution, weight percent	
C_{14}	1
C_{15}	27
C_{16}	29
C_{17}	28
C_{18}	14
C_{19}	1
Average molecular weight	228
Color, Saybolt	+3

TABLE V
Formulations Used for Evaluations in Heavy-Duty Detergents

Shortened formula	Complete formula
25/0 or 20/0	25% or 20% Test surfactant 0% Additive 40% Tripolyphosphate 7% Silicate 1% CMC (carboxymethyl cellulose) 19% or 24% inorganic sulfate 8% Water
18.5/1.5	18.5% Test surfactant 1.5% LIPA (lauric isopropanolamide) 45% Tripolyphosphate 5% Silicate 1% CMC (carboxymethyl cellulose) 20% Inorganic sulfate 9% Water
7.5/9.5	7.5% Test surfactant 9.5% Tallow alcohol sulfate 2% LEA (lauric ethanolamide) 1% Lauryl alcohol 45% Tripolyphosphate 5% Silicate 1% CMC (carboxymethyl cellulose) 21% Inorganic sulfate 8% Water

Color was usually measured by the tristimulus method using 2% solutions (14,15). In some cases Klett colors were determined using a Klett-Summerson photoelectric colorimeter.

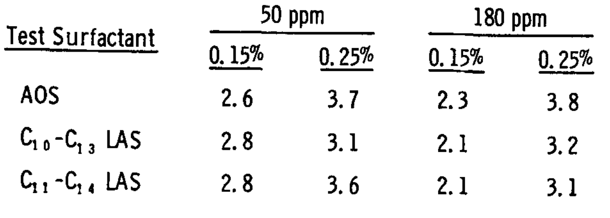
Oil determinations were made by extraction of the oil with 30–60C petroleum ether from a 70–75% ethanol-water solution of the surfactant followed by removal of solvent by heating to constant weight. With AOS, it is necessary to perform the deoiling step with quantities such that the concentration of surfactant in the ethanol-water solution is less than 7% and preferably around 5% in order to extract all of the oil.

Sodium sulfate content was measured by barium perchlorate titration after treatment of a solution of the sample with Dowex 50X8 or Amberlite IR-120 ion exchange resin.

Storage stability tests were run in an accelerated test by storing 5–10 samples of dried powder in a 70C oven. The test samples were periodically smelled and rated on a comparative scale by a panel of individuals. An identical set of samples was kept in the dark at room temperature for control purposes.

Performance Testing

The hand dishwashing foam test is similar to a published one (16) and employs plates uniformly soiled with a shortening soil to which has been added a colored dye. At a temperature of 115F and a surfactant formula concentration of 0.15%, plates are washed until no more foam remains in the dishpan. Two controls are run in each test. Normalization of results by use of these two controls greatly reduces the effect of unavoidable random variations in the test. The data given in this paper are based on multiple runs, more runs for the C_{15}–C_{18} AOS than for the single-carbon species. For the former,



Test Surfactant	50 ppm		180 ppm	
	0.15%	0.25%	0.15%	0.25%
AOS	2.6	3.7	2.3	3.8
C_{10}-C_{13} LAS	2.8	3.1	2.1	3.2
C_{11}-C_{14} LAS	2.8	3.6	2.1	3.1

The foam level was satisfactory in all cases.

FIG. 19. C_{15}–C_{18} AOS detergency in Westinghouse front-loading washer. 12/4.4 tallow soap low foaming formulation.

TABLE VI
Formulations Used for Evaluations in Light-Duty Liquid Detergents

Shortened formula	Complete formula
18/12/6	18% Test surfactant
	12% Ammonium C_{12}–C_{15} primary alcohol ethoxy sulfate
	6% LMDEA (Lauric myristic diethanolamide)
	12% Ethanol
	2.5% Sodium xylene sulfonate
20/5	20% Test surfactant
	5% Coco-dimethylamine oxide
	10.5% Ethanol

95% confidence limits are about ±1.5 plates; and for the latter, they are slightly less than ±2 plates.

The natural soil detergency test employs the Terg-O-Tometer (Model BD-101, U.S. Testing Company) to wash at 120F cotton swatches soiled with natural skin sebum. Soil removal is measured by reflectance (Photovolt Model 610 reflection meter with an external, high sensitivity galvanometer, Chevron Research Company Electronics Laboratory). The results are normalized after three soil/wash cycles through the use of two controls, one chosen to give good cleaning (assigned value of 6 relative detergency units) and the other poor cleaning (assigned value of 2). Using these internal standards, many random fluctuations in soil removal results are overcome. Tests using cotton swatches soiled with Foster D. Snell soil are run at 130F in the same equipment, and the results are normalized in the same manner. Relative detergency values have 95% confidence limits of about ±0.4 unit.

Foamability and detergency in the front-loading washer are measured in a Westinghouse machine containing 6 lb of clean shop towels and ten 16-in. × 36-in. × 3 ml polyethylene sheets in 26 liters of water containing 40 ppm lard oil. Since the good and poor standards used as controls are high foaming formulations, they are of necessity run in a Kenmore top-loading machine. The normalization procedure is then not as direct as in the case of the Terg-O-Tometer work, but it does tend to minimize the effect of variations in soil composition.

Formulations used are given in detail in Tables V and VI. Throughout the work, Oronite Alkane 1056 and Alkane 1060 sulfonates were used as examples of C_{10}–C_{13} and C_{11}–C_{14} LAS, respectively.

ACKNOWLEDGMENTS

The personnel of the General Chemical Division, Allied Chemical Company, made available to us their semicommercial scale sulfonation facilities. G. L. Woo performed the hydrogenation experiment; Oronite Division, Chevron Chemical Company, provided continued support of this work.

REFERENCES

1. Abrams, A., E. J. Carlson, E. E. Gilbert and H. R. Nychka, JAOCS *37*, 63 (1960).
2. Bordwell, F. G., and C. S. Rondestvedt, J. Am. Chem. Soc. *70*, 2429 (1948).
3. Püschel, F., and C. Kaiser, Ber. *97*, 2903, 2917, 2926 (1964).
4. Bordwell, F. G., F. B. Colton and M. Knell, J. Am. Chem. Soc. *76*, 3950 (1954).
5. Bordwell, F. G., C. M. Suter, J. M. Holbert and C. S. Rondestvedt, Ibid. *68*, 139 (1946).
6. Bordwell, F. G., R. D. Chapman and C. E. Osborne, Ibid. *81*, 2002 (1959).
7. Bordwell, F. G., M. L. Peterson and C. S. Rondestvedt, Ibid. *76*, 3945 (1954).
8. Bordwell, F. G., and M. L. Peterson, Ibid. *76*, 3952 (1954).
9. England, D. C., M. A. Dietrich and R. V. Lindsey, Ibid. *82*, 6181 (1960).
10. von Rudloff. E., JAOCS *33*, 126 (1956).
11. Püschel, F., and C. Kaiser, Ber. *98*, 735 (1965).
12. Subcommittee on Biodegradation Test Methods, SDA, JAOCS *42*, 986 (1965).
13. Liddicoet, T. H., and S. A. Olund, JAOCS *40*, 5 (1963).
14. House, R., and J. L. Darragh, Anal. Chem. *26*, 1492 (1954).
15. Hardy, A. C., "Handbook of Colorimetry," Cambridge, Massachusetts, MIT, The Technology Press, 1936.
16. Spangler, W. G., JAOCS *41*, 300 (1964).

[Received May 6, 1966]