USE OF LIQUID SULFUR TRIOXIDE AS A SULFONATING AGENT FOR ORGANIC COMPOUNDS

BY

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ABSTRACT

Dodecylbenzene was sulfonated with SO_3 and evaluated as to ash, sodium sulfate, degree of sulfonation, and was also compared with an oleum sulfonation. Its homolog, octadecylbenzene, was made, sulfonated, and found to be less effective as a wetting agent.

Two-ethylhexyl cinnamate, oleic acid, and propyloleate were also sulfonated with good yields and evaluated.

Yields in the sulfonation of Di-2-ethylhexyl maleate were very low. There was evidence of the SO_3 splitting the ester and oxidizing it to maleic acid.

The reduction of 9-octadecenophenone, according to Clemmenson's Method, led to the formation of a polymer.

APPROVAL OF THESIS

FOR

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BY

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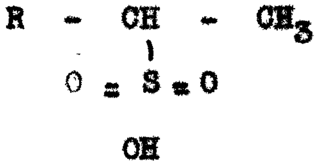
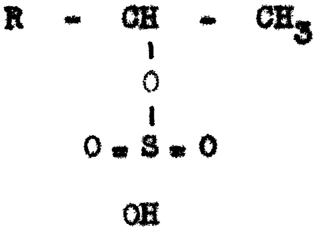
In the treatment of organic compounds, the action of sulfuric acid does not always lead to the formation of sulfonated derivatives. In the case of olefinic compounds, the sulfated derivative is often formed. On the other hand, the use of sulfur trioxide usually leads to the formation of sulfonated derivatives. It will be well to distinguish first between true sulfonated compounds and compounds that are more or less sulfated, or complexes formed by the action of sulfuric acid on an organic compound.

A sulfonated derivative is a body having in its molecule a radical, SO_3H, in which the hexavalent sulfur atom is attached directly to a carbon atom in the principal chain as follows:



$$\begin{array}{ccccc} R & - & CH & - & CH_3 \\ & & | & & \\ & O = & S & = O & \\ & & OH & & \end{array}$$

On the other hand, a derivative called, "sulfated", also contains a SO_3H group, but the hexavalent sulfur atom is attached to an oxygen atom in the principal chain:



$$\begin{array}{ccccc} R & - & CH & - & CH_3 \\ & & | & & \\ & & O & & \\ & & | & & \\ & O = & S & = O & \\ & & OH & & \end{array}$$

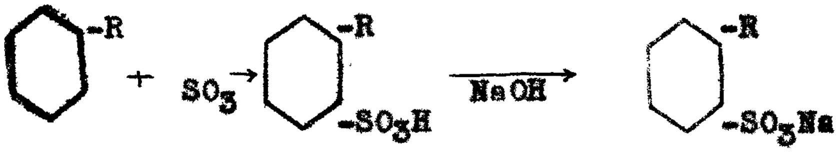
(Continued)

A sulfated product is, in fact, an alkaline salt of a sulfuric acid ester. As the functional ester is less stable to hydrolysis, it seems more desirable in order to obtain products with good stability to acids, to make the sulfonates.

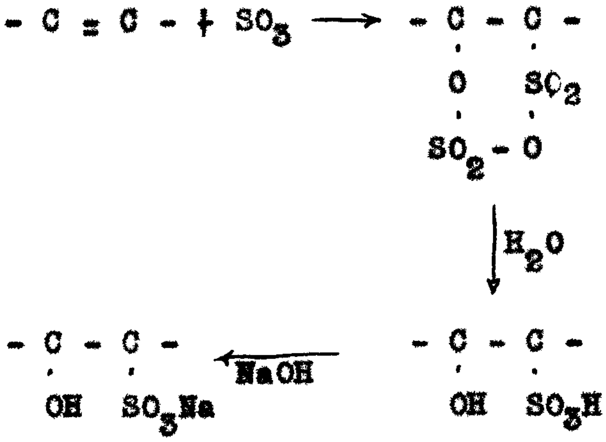
The purpose of this paper is to determine what advantage, if any, sulfur trioxide has as a sulfonating agent over sulfuric acid or oleum.

This study will consider two types of reactions that sulfur trioxide can undergo. These may be shown as follows:

1.



2.



Exhaustive studies have been made on the above types using concentrated sulfuric acid and oleum. However, very little has been done with liquid sulfuric anhydride.

Sulfuric anhydride is theoretically the most active reagent for sulfonation, but its destructive action on organic matters and the violence of its reaction have limited its use to reactions in which it can be employed in a diluted form. Its instability is, likewise, a limiting factor.

The General Chemical Company has a method of stabilizing sulfuric anhydride by adding less than 0.5% of a stabilizer. The product is sold under the name of "Sulfan". Sulfan retains its liquid form and can be diluted in a solvent or in an inert gas so that the rate of sulfonation can be controlled as desired.

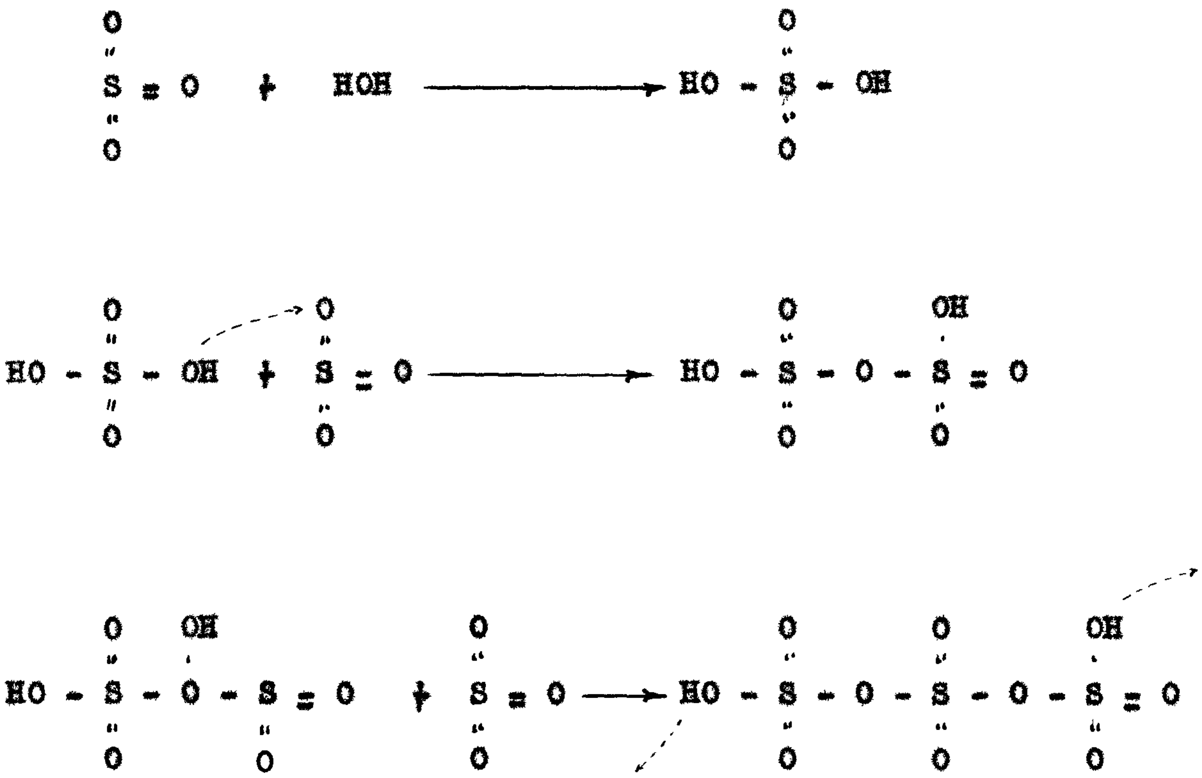
Sulfan must be carefully handled and not allowed to come in contact with atmospheric moisture, otherwise polymerization takes place, leading to the formation of the beta form of SO_3. Sulfan, as supplied from General Chemical Company, was used in all the experiments in this paper.

Since the proper sulfonating procedure is very important, consideration was given to it with respect to:

1. Temperature of reaction
2. Type of agitation
3. Ratio of sulfur trioxide to product being sulfonated
4. Rate of addition of sulfur trioxide
5. Method of addition of SO_3.

Dr. Gilbert and his co-workers of General Chemical Company have worked out a general procedure by vaporizing the SO_3 and using air as a diluent. In all my experiments I used this general procedure. See attached sketch.

MECHANISM IN THE POLYMERIZATION OF SULFUR TRIOXIDE



$$\overset{O}{\underset{O}{S}} = O + HOH \longrightarrow HO - \overset{O}{\underset{O}{S}} - OH$$

$$HO - \overset{O}{\underset{O}{S}} - OH + \overset{O}{\underset{O}{S}} = O \longrightarrow HO - \overset{O}{\underset{O}{S}} - O - \overset{OH}{\underset{O}{S}} = O$$

$$HO - \overset{O}{\underset{O}{S}} - \overset{OH}{O} - \underset{O}{S} = O + \overset{O}{\underset{O}{S}} = O \longrightarrow HO - \overset{O}{\underset{O}{S}} - O - \overset{O}{\underset{O}{S}} - O - \overset{OH}{\underset{O}{S}} = O$$

CALIBRATION OF ORIFICE IN AIR LINE

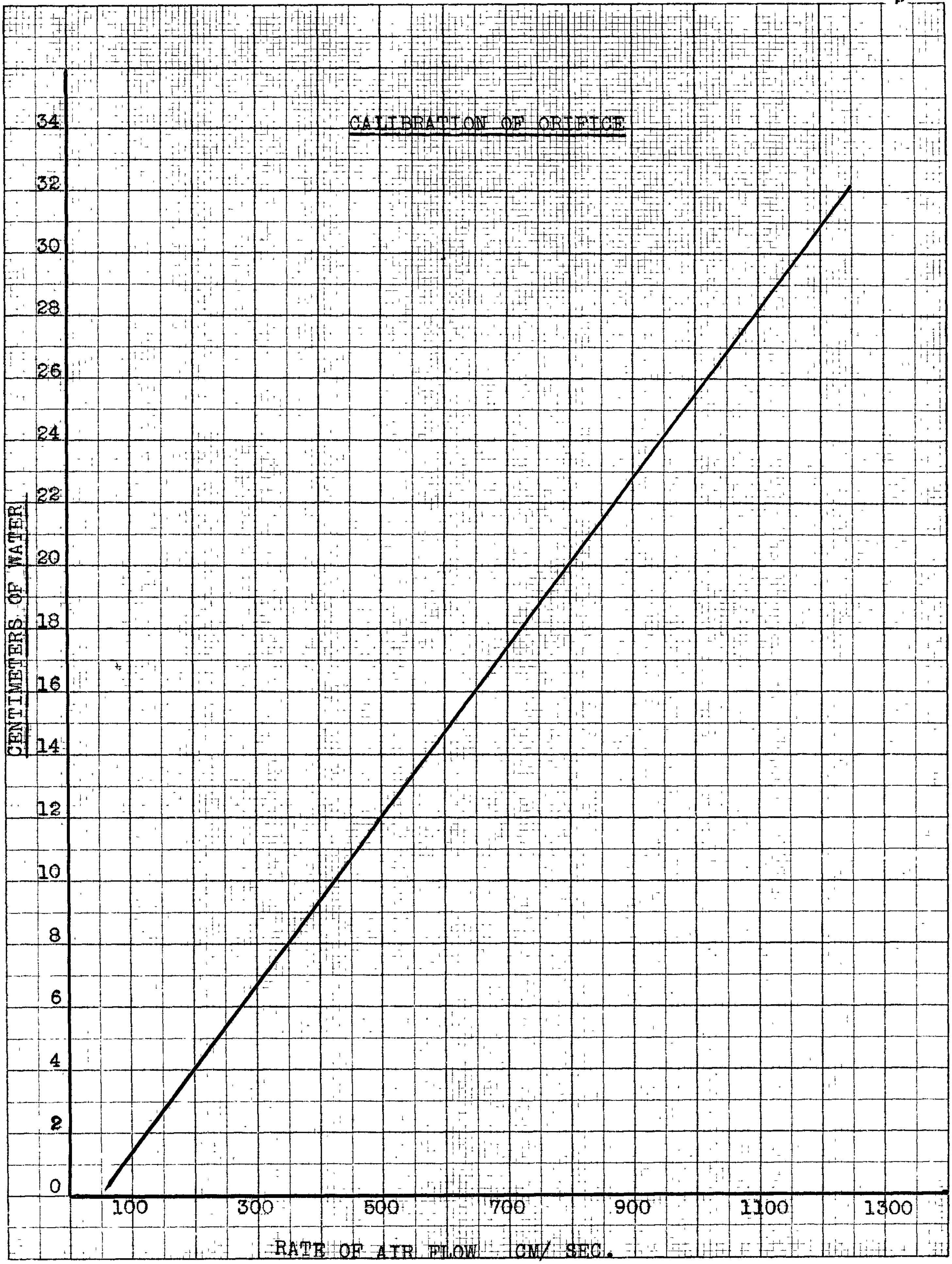
An orifice was made by heating a small piece of glass tubing near the center of its length, while the ends were pulled just far enough to make the ratio of the diameter of the orifice to the diameter of the tube approximately 1-10. The orifice was then mounted on a panelboard with U-tube connections as shown in the accompanying diagram.

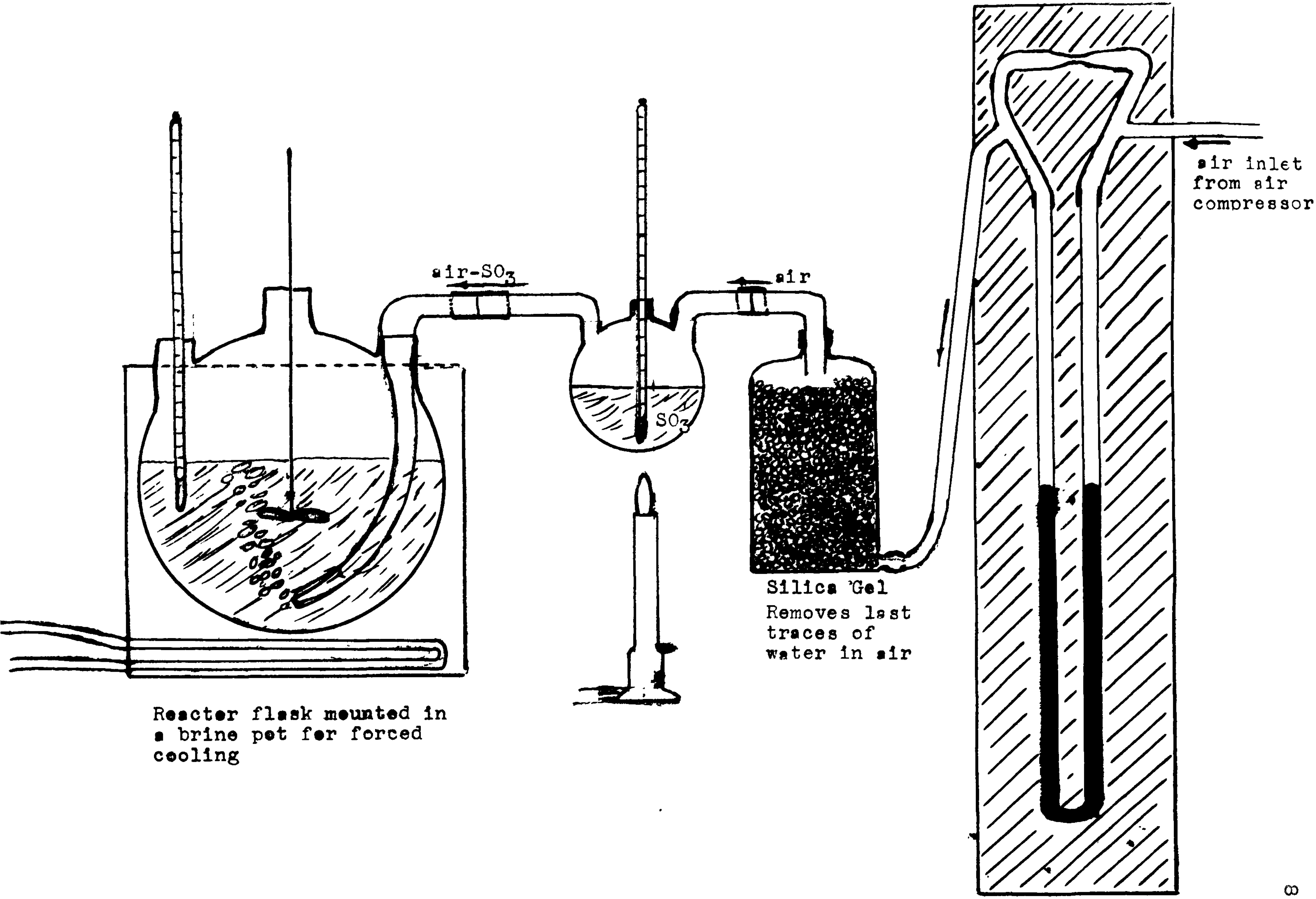
A five-gallon jug was then fitted with a water inlet line and an air vent. The air vent was connected to the air manometer. By filling the jug with water at various rates and letting the vented air pass through the manometer, it was possible to obtain a calibration curve of pressure drop versus air rate. This calibration was used to determine the volume of air used in sulfonating with Sulfan.

Calibration Data on Curve

RATE		cc. H_2O
lbs. per min.	cc. per sec.	in Manometer
24	180	2
28	214	4
38	287	6
48	361	8

Calibration curve is on the following page.


CALIBRATION OF ORIFICE
CENTIMETERS OF WATER
34
32
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
100
300
500
700
900
1100
1300
RATE OF AIR FLOW CM/ SEC.



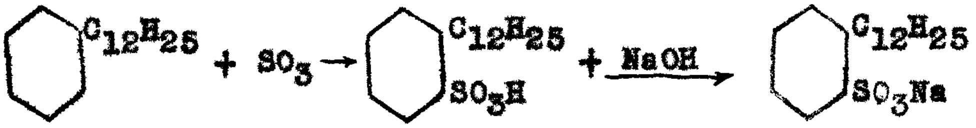
Silica Gel
Removes last traces of water in air

Reacter flask mounted in a brine pot for forced cooling

SKETCH OF EQUIPMENT USED IN SULFONATING WITH LIQUID SO_3 -SULFAN

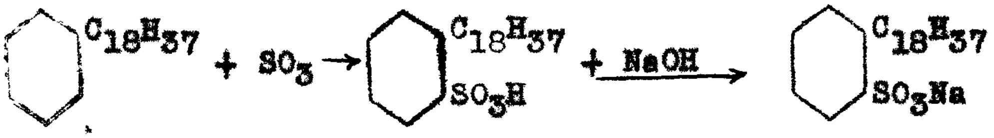
The Products and Reactions Studied were as Follows:

1. Sulfonation of Dodecylbenzene

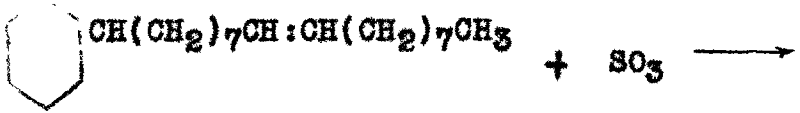


Reaction number one has been studied extensively with good yields. It was the good results on reaction number one that suggested a stody of the following reactions:

2. Sulfonation of Octadecylbenzene

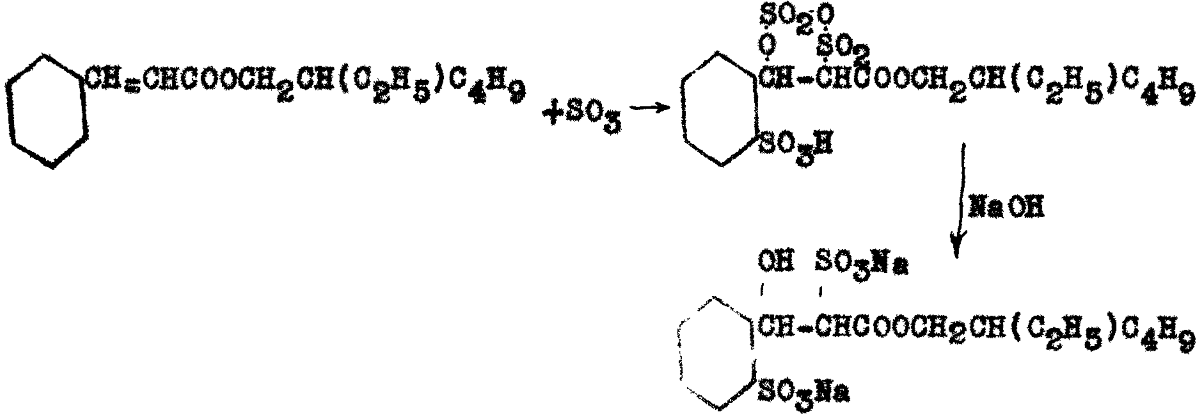


3. Sulfonation of 9-Octadecenylbenzene



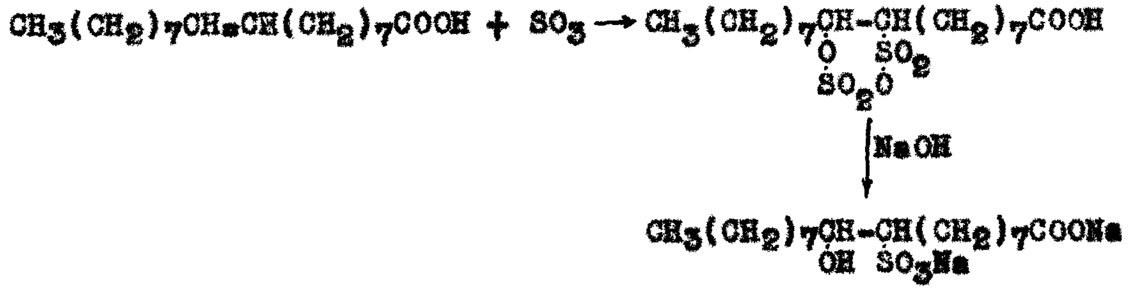
This reaction could not be studied since 9-Octadecenylbenzene could not be made from the reduction of 9-Octadecenophenone.

4. Sulfonation of 2 Ethylhexyl Cinnamate



(Continued)

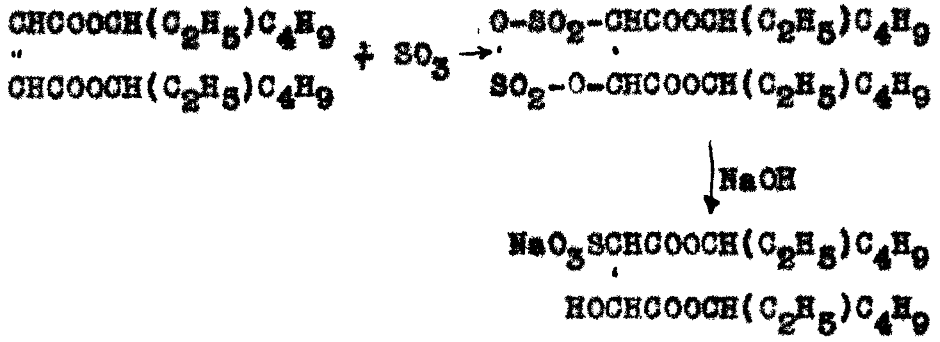
5. Sulfonation of Oleic Acid



$$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH + SO_3 \rightarrow CH_3(CH_2)_7\underset{\substack{O\\SO_2}}{CH}-\underset{\substack{SO_2\\O}}{CH}(CH_2)_7COOH$$

$$\xrightarrow{NaOH} CH_3(CH_2)_7\underset{OH}{CH}-\underset{SO_3Na}{CH}(CH_2)_7COONa$$

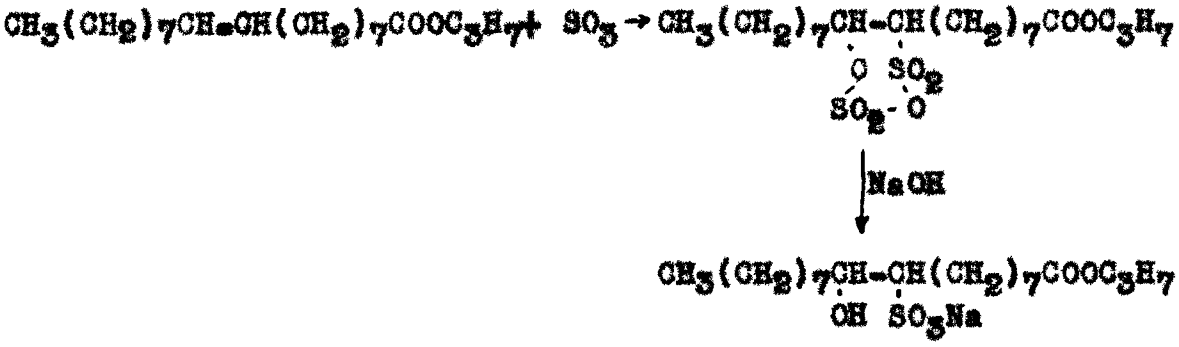
6. Sulfonation of Di-2-Ethylhexyl Maleate



$$\begin{array}{l}CHCOOCH(C_2H_5)C_4H_9\\ \parallel\\ CHCOOCH(C_2H_5)C_4H_9\end{array} + SO_3 \rightarrow \begin{array}{l}O-SO_2-CHCOOCH(C_2H_5)C_4H_9\\ SO_2-O-CHCOOCH(C_2H_5)C_4H_9\end{array}$$

$$\xrightarrow{NaOH} \begin{array}{r}NaO_3SCHCOOCH(C_2H_5)C_4H_9\\ HOCHCOOCH(C_2H_5)C_4H_9\end{array}$$

7. Sulfonation of Propyloleate



$$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOC_3H_7 + SO_3 \rightarrow CH_3(CH_2)_7\underset{\substack{O\\SO_2}}{CH}-\underset{\substack{SO_2\\O}}{CH}(CH_2)_7COOC_3H_7$$

$$\xrightarrow{NaOH} CH_3(CH_2)_7\underset{OH}{CH}-\underset{SO_3Na}{CH}(CH_2)_7COOC_3H_7$$

ANALYSIS OF END PRODUCT

In analyzing the end product I studied the following:

1. Disposal of the spent acid.
2. Percentage yield.
3. Color of end product as compared with a sulfuric acid sulfonation of same product.
4. Percentage of ash as compared with a sulfuric acid sulfonation.
5. Comparative ease of addition of SO_3 to unsaturated aliphatic or to an aromatic compound.

SULFONATION OF DODECYLBENZENE

The dodecylbenzene used in these experiments was purchased under the trade names "Neolene" from Sharples, and "Oronite" from Oronite Chemical Company. A considerable amount of work has been done with this compound by General Chemical Company since it sulfonated very readily with sulfur trioxide. The purpose here was to determine what advantages, if any, there were in this type of sulfonation.

Six runs were made and the products analyzed and compared with dodecylbenzene sulfonated with 20% oleum.

The technique in sulfonating I found to be very important as to the type of agitation, method of bubbling, and ratio of air to SO_3. Several types of agitation and bubbling were tried, and I found the best results were obtained when I took a glass rod and flattened the end just enough so that the rod would fit through a 29/42 ground-glass fitting. The position of the agitator was directly at the end of the bubbler, and the agitator was coupled to a high-speed motor. By this method I was able to obtain better color than when I used a bubbler made up of fine pinholes. The bubbler of fine pinholes often caused a back pressure which necessitated lowering the rate of air. When the air rate was lowered the product darkened, since the ratio of air to SO_3 was lowered.

PREPARATION OF DODECYLBENZENESULFONIC ACID

A three-liter flask was set up in a brine bath equipped with cooling coils so that the temperature of the brine was kept constant at approximately zero degrees Centigrade. The flask was equipped with an agitator, thermometer, and a bubbling tube. The first trials were made by bubbling the gas through the open end of the glass tube. Later trials were made with bubblers that consisted of tine pinholes in a glass tubing. Eight hundred and forty grams of anhydrous dodecylbenzene were added to the flask.

To the right of the brine kettle, another three-neck flask was set up, and 322 grams of sulfur trioxide were added to it. It was equipped with a thermometer and two ground-glass tubes. One tube was connected to the bubbler in the reaction flask, and the other end was connected to a glass bottle filled with silica gel. Air from a compressor was passed through an orifice with a manometer attached and then into the bottle of silica gel to remove all traces of water.

The dodecylbenzene in the reaction flask was pre-cooled to 15°C, and dry air was bubbled through at the rate of 940 cc per second. The sulfur trioxide in the second flask was heated with a low flame from a bunsen burner to 25°C. Sulfur trioxide was bubbled into the dodecylbenzene in vapor form. It took one-half hour to bubble the sulfur trioxide into the dodecylbenzene. The temperature of the reaction flask rose slowly to 30°C during the half hour.

The dodecylbenzene sulfonate was then added with cooling to a two-liter flask containing a 50% solution of sodium hydroxide, and the temperature of the neutralization was not permitted to go above 40°C.

The sodium salt of dodecylbenzenesulfonic acid was a 50% slurry.

ANALYTICAL PROCEDURES USED IN ANALYZING SULFONATES

Sodium Sulfate Content

A representative sample of the sodium sulfonate of dodecylbenzene was mixed with 95% denatured ethyl alcohol at 125 to 130°F. Sodium sulfate was precipitated from the cooled alcohol solution of the sulfonate, washed twice with alcohol, and decanted. The precipitate was filtered into a tared Gooch crucible, washed with alcohol, and dried for one-half hour at 220 to 230°F.

$$\%\ \text{Sodium sulfate} = \frac{\text{Wt. of Ppt.} \times 100}{\text{Sample Weight}}$$

Percent Residual Oil

An accurately-weighed sample containing approximately three grams of sulfonate in 50 ml of distilled water was placed in an Erlenmeyer flask. Then 50 ml of ethyl alcohol were added and this was cooled to room temperature. Fifty ml. of 50% alcohol solution were added, then 30 ml of petroleum ether were added and shaken vigorously for 30 seconds. The stopper was cautiously removed and the two phases allowed to separate completely. The addition of a small amount of sodium sulfate crystals aided in breaking the emulsion. The ether layer was siphoned into a tared 250 ml extraction flask and the extraction repeated with small amounts of ether at least four times.

The ether was evaporated from the extraction flask on a steam bath and brought to constant weight. When the loss did not exceed 10 mg, the weight was considered constant.

EVALUATION OF WETTING PROPERTIES

American Standards Association Test Designation L14.11-1949

A weighted cotton test skein was dropped into a tall cylinder containing a water solution of a wetting agent. The time required for a string stirrup connecting the weight and the skein to relax is recorded as the sinking time.

For a determination, a 5.00-gram skein of yarn was folded enough times to form a loop 18 inches around. A 54-inch skein was formed into an 18-inch loop with three folds. The hook with its anchor was fastened at one end of the folded skein, and the skein was cut through with shears at the opposite end. The cut skein was drawn through the fingers in order to make it more compact. Any threads which were tied around the skein to correct its weight were folded into the skein near the hook. The skein was held with one hand with the anchor dangling into the wetting solution contained in the 500 ml graduated cylinder. A stop watch held in the other hand was started just as the skein was released into the solution and was stopped when the buoyant skein definitely started to sink to the bottom of the cylinder.

(The skein, before sinking, must be entirely covered with solution; and yet it must possess enough buoyancy from the air within the yarn to keep the linen thread taut between the anchor and the hook.)

SUMMARY OF DATA ON THE SULFONATION OF DODECYLBENZENE WITH LIQUID SO_3

Run No.	#1	#2	#3	#4	#5	#6	#7
Oil Used	Neolene	Oronite	Neolene	Neolene	Neolene	Oronite	Oronite
Agent Used	Sulfan	Sulfan	Sulfan	Sulfan	Sulfan	Sulfan	20% Oleum
Moles of Oil		3.37	3.37	2	2	2	2
Moles of SO_3	2.2	4.0	4.0	2	2.4	2.4	4.2 H_2SO_4 1.25 SO_3
Wt. Ratio SO_3 to Oil	1-2.86	1-2.6	1-2.6	1-3.13	1-2.6	1-2.6	1-1
% Excess SO_3	10	20	20	0	20	20	35
Grams Oil	500	840	840	500	500	500	500
Grams SO_3	175	322	322	160	192	192	500
SO_3 Charging Time (Min.)	30	45	40	180	160	150	30
SO_3 Contact Time	90	55	45	190	170	160	60
Average Reaction Temp.	62°C	35	45	50	66	50	55
Ratio of SO_3 to Air	1-5	1-9.5	1-8.75	1-6	1-5	1-4.4	
Neutralization Reagent	NaOH	NaOH	NaOH	NaOH	NaOH	NaOH	NaOH

PRODUCT ANALYSIS OF THE SULFONATION OF DODECYLBENZENE WITH LIQUID SO_3

Run No.	#1	#2	#3	#4	#5	#6	#7
Ash		9.1	8.2	10.5	11.4	9.2	20.7
pH	7-8	7-8	7-8	7-8	7-8	7-8	7-8
% Water	44.7	52.3	48.5	49.0	48.1	49.2	50.
% Solids	55.3	47.7	51.5	51.0	51.9	50.8	50.
% $NaSO_4$ on Solids	4.1	5.0	3.8	5.0	6.3	6.3	9.44
% Oil on Solids	10.9	3.1	2.3	1.6	1.2	1.8	3.32
% Sulfonated Oil on Solids	85.0	91.9	93.9	93.4	92.3	91.9	87.24
Color	Dark	Light Brown	Light Brown	Very Light Brown	Light Brown	Light Brown	Light Brown
Penetration* (sec.)	10	10	11	16	10	10	15

*Evaluation of penetration according to American Standards Association: Test Designation L14.11-1949.

ADVANTAGES OF THE USE OF SULFAN

ANALYSIS OF DATA ON DODECYLBENZENE SULFONATES

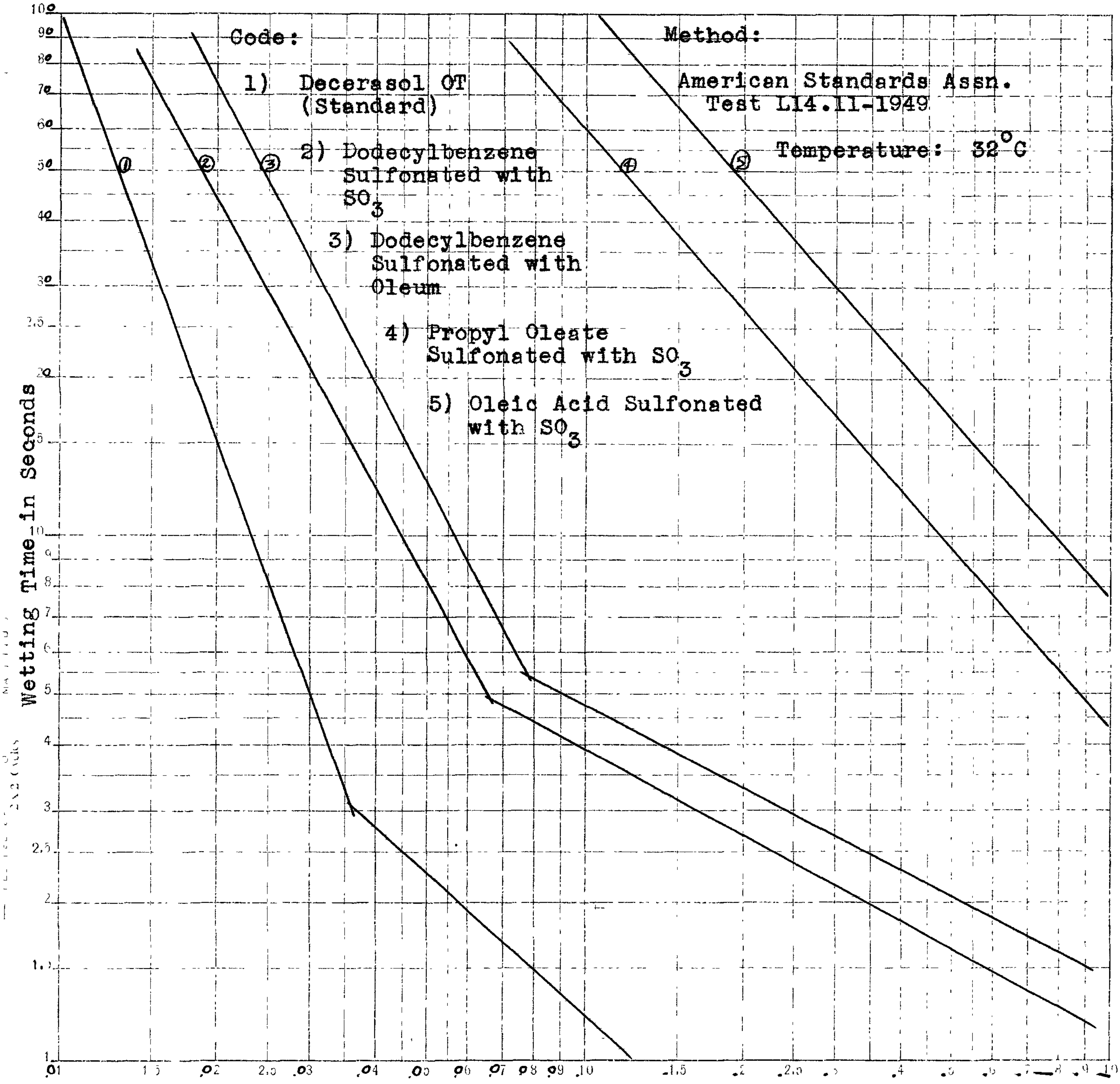
1. Use of SO_3 avoids the spent acid which is present in an oleum sulfonation. In sulfonating with oleum, a spent acid is left, necessitating a disposal problem in large scale operation. Sulfonating with sulfur trioxide is done on an equimolal basis, and there is very little excess acid to neutralize. Theoretically, the only caustic needed should be that necessary to neutralize the dodecylbenzenesulfonic acid.

2. Use of SO_3 lowers the amount of sodium sulfate and, consequently, the amount of ash in the end product. The ash, as shown in the fore-going data, was reduced from approximately 20% to 10%.

3. The percent sulfonation was increased as can be seen by the lowering of the amount of unsulfonated oil.

4. The penetrating properties of the end product were improved as can be seen by the attached graph.

PENETRATION CURVES



Percent Concentration Based on 100% Products

SULFONATION OF OCTADECYLBENZENE

Since the calcium salt of dodecylbenzenesulfonic acid is soluble in water, dodecylbenzene sulfonates can be used in water that has a relatively high mineral content. This product also has excellent penetrating properties. In view of this its homolog, octadecylbenzene, should be expected to have favorable characteristics also. Therefore, the latter product was made and tried, since it is cheaper and more available.

Using stearic acid as a basic raw material, octadecylbenzene was made and sulfonated with SO_3 as follows:

$$3\ C_{17}H_{35}COOH + PCl_3 \longrightarrow 3\ C_{17}H_{35}COCl + P(OH)_3$$

$$C_{17}H_{35}COCl + C_6H_6(+ AlCl_3) \longrightarrow C_{17}H_{35}COC_6H_5 + HCl$$

$$C_{17}H_{35}COC_6H_5 + \text{Zn Amalgam} \cdot HCl \longrightarrow C_6H_5C_{18}H_{37}$$

Clemmenson Reduction

$$C_6H_5C_{18}H_{37} + SO_3 \longrightarrow C_6H_4(SO_3H)C_{18}H_{37}$$

$$C_6H_4(SO_3H)C_{18}H_{37} + NaOH \longrightarrow C_6H_4(SO_3Na)C_{18}H_{37} + H_2O$$

PREPARATION OF OCTADECANOYL CHLORIDE USING PCl_3

A three-neck, two-liter flask was fitted with an agitator, addition funnel, and condenser with a calcium chloride tube. The flask was placed in a water bath in a hood, and 986 grams of stearic acid were added to it. The acid was kept at 70°C until 177 grams of fresh PCl_3 were added drop-wise over a sixty-minute period. After this addition, the mixture was held at 80°C with agitation for three hours on the water bath. At the end of this period, the contents were transferred to a separatory funnel and the phosphorous acid allowed to settle to the bottom. After standing overnight, the phosphorous acid was drawn off. The residual portion was stearoyl chloride with a melting point of 23°C.

PREPARATION OF STEAROPHENONE

A two-liter, three-neck flask was fitted with a thermometer, dropping funnel, and a reflux condenser with a calcium chloride tube. The flask was placed on a water bath under a hood, and 240 grams of anhydrous $AlCl_3$ and 800 cc of anhydrous benzene were added to it. The mixture was warmed slightly, and a solution containing 216 grams of stearoyl chloride in 500 cc of anhydrous benzene was added carefully over a two-hour period. The reaction was gentle and no cooling was necessary. After the addition was complete, the dropping funnel was removed and an agitator put in its place. The mixture was then stirred and heated to a reflux temperature of 80°C for a half-hour and then cooled to room temperature. The contents were then transferred to a two-liter beaker, which was placed in a water bath, and 400 ml of 3-N-hydrochloric acid were added with extreme care. After the addition of hydrochloric acid, the entire acid mixture was transferred to a separatory funnel and allowed to separate. The acid layer was removed, and the benzene layer was washed with water several times. The excess benzene was then distilled off. To remove the excess acid, the reaction product was washed with hot water containing enough sodium hydroxide to make it permanently alkaline. It was then washed several times until it was neutral to methyl orange. The reaction product, stearophenone, had a melting point of 42 to 43°C.

REDUCTION OF STEAROPHENONE

Two hundred grams of mossy zinc were weighed into a two-liter, three-necked flask. The metal was amalgamated by treatment with 15 cc of mercuric chloride, 150 cc water, and 10 cc of hydrochloric acid. This was shaken for ten minutes and the liquor decanted. To the zinc amalgam was added sufficient concentrated hydrochloric acid to cover about one-half of it, plus 100 cc of water. To this was added a solution of 250 grams stearophenone in 750 cc of xylene. The mixture was heated under reflux for seven hours, during which time hydrogen chloride was added to the flask to replace losses. The xylene layer was then separated, the solvent removed, and the product distilled, b.p. 220-235°/5 mm. A residue of about 30 grams of a heavy oil was discarded.

The distillate was dissolved in 750 cc of xylene and treated with another portion of zinc amalgam and hydrochloric acid as described above. The product isolated, b.p. 195-205°/4 mm., m.p. 33°, weighed 190 grams (77%). Crystallization of the n-octadecylbenzene from ether yields a product of m.p. 35-36°.

SULFONATION OF OCTADECYLBENZENE

The sulfonation of octadecylbenzene was carried out according to the same procedure as was used in sulfonating dodecylbenzene on Pages 12 and 13. One hundred grams of octadecylbenzene were sulfonated with 33 grams of sulfur trioxide (equimolal ratio). The time required for the addition of the acid was 45 minutes, and the total time in the acid was 60 minutes. The sulfonate was neutralized with 50% sodium hydroxide to a pH of 7.

The percent sulfonation was 27.6 calculated from the amount of unsulfonated oil by analysis. A 1% solution had no wetting properties according to the method described on Page 16. The ash and sodium sulfate were large, since the unreacted acid formed sodium sulfate when neutralized. The amount of unsulfonated oil was 72.4%. This made it impossible to obtain an accurate reading on the wetting properties.

SULFONATION OF 9-OCTADECENYLBENZENE

An attempt was made to make 9-octadecenylbenzene, sulfonate it, and compare it with octadecylbenzene. I was able to make 9-octadecenophenone. However, on the reduction according to Clemmenson's Method using zinc and hydrochloric acid, the product polymerized.

The expected synthesis would have been:

$$3CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH + PCl_3 \rightarrow 3CH_3(CH_2)_7CH{=}CH(CH_2)_7COCl$$

$$CH_3(CH_2)_7CH{=}CH(CH_2)_7COCl + C_6H_6 \xrightarrow{(AlCl_3)} C_6H_5CO(CH_2)_7CH{=}CH(CH_2)_7CH_3$$

$$C_6H_5CO(CH_2)_7CH{=}CH(CH_2)_7CH_3 \xrightarrow{Zn\ .\ HCl} C_6H_5CH_2(CH_2)_7CH{=}CH(CH_2)_7CH_3$$

The ketone was actually made, although its reduction was not successful. A description of the preparation of the ketone follows.

PREPARATION OF 9-OCTADECENOYL CHLORIDE USING PCl_3

A three-neck, two-liter flask was fitted with an agitator, addition funnel, and a condenser with a calcium chloride tube. The flask was placed in a water bath in a hood, and 986 grams of oleic acid were added to it. The acid was kept at 30°C until 177 grams of fresh PCl_3 were added drop-wise over a 60-minute period. After this addition, the mixture was held at 80°C with agitation for three hours on a water bath and then allowed to separate overnight in a separatory funnel. The phosphorous acid settled to the bottom and was drawn off. The remaining portion was 9-octadecenoyl chloride with a melting point below 15°C.

PREPARATION OF 9-OCTADECENOPHENONE

A two-liter, three-neck flask was fitted with a thermometer, dropping funnel, and a reflux condenser with a calcium chloride tube. The flask was placed on a water bath under a hood, and 240 grams of anhydrous $AlCl_3$ and 800 cc of anhydrous benzene were added to it. The mixture was warmed slightly, and a solution containing 216 grams of 9-octadecenoyl chloride in 500 cc of anhydrous benzene was added carefully over a two-hour period. The reaction was gentle and no cooling was necessary. After the addition was complete, the dropping funnel was removed and an agitator put in its place. The mixture was stirred and heated to a reflux temperature of 80°C for two hours and then cooled to room temperature. The contents were then transferred to a two-liter beaker, which was placed in a water bath, and 400 ml of 3-N-hydrochloric acid were added with extreme care. After the addition of hydrochloric acid, the entire mixture was transferred to a separatory and allowed to separate. The acid layer was removed and the benzene layer washed with water several times. It was then agitated in the presence of an excess of sodium hydroxide, making it permanently alkaline. It was then washed until neutral to methyl orange. The reaction product, 9-octadecenophenone, had a melting-point less than 5°C.

REDUCTION OF 9-OCTADECENOPHENONE

Two hundred grams of mossy zinc were weighed into a two-liter, three-neck flask. The metal was amalgamated by treatment with 15 cc of mercuric chloride, 150 cc water, and 10 cc of hydrochloric acid. This was shaken for ten minutes and the liquor decanted. To the zinc amalgam was added sufficient concentrated hydrochloric acid to cover about one-half of it, plus 100 cc of water. To this was added a solution of 250 grams of 9-octadecenophenone in 750 cc xylene. The mixture was heated under reflux for seven hours, during which time hydrogen chloride was separated, the solvent removed and re-dissolved in petroleum ether, and added to a beaker containing a solution of sodium hydroxide. This was stirred for one-half hour until the residual acid was neutralized. It was then washed until neutral to methyl orange. It was then separated and the ether distilled. The product would not distill at 250°C and 14 mm.

An iodine number, which is the percentage of iodine absorbed by a substance, was run and found to be 14.8%. The theoretical value for 9-octadecylbenzene is 78%.

A molecular weight determination was run by the method of freezing point lowering, using benzene and a Bechmann Thermometer. The molecular weight was 842. The theoretical molecular weight is 328.

(Continued)

In view of these findings, it may be seen that 9-octadecylbenzene cannot be made from 9-octadecenophenone using the Clemmenson Reduction. The product polymerized at the double bond as is indicated by the lowering of the iodine number, and the increase in the molecular weight. A lower iodine number indicates that the number of double bonds has decreased. This is logical since polymerization takes place at the double bond.

PREPARATION OF 2-ETHYLHEXYL CINNAMATE

A three-neck, two-liter flask was set up with a water-trap, condenser, agitator, and thermometer. Into the flask was weighed 436 grams of cinnamic acid and 383 grams of 2-ethylhexanol (equimolal ratio) with 160 grams benzol and 3 grams of c.p. sulfuric acid. The mixture was heated over a flame with agitation until 47 cc of water were collected in the water trap. During the reaction, the benzol was refluxed back into the flask, and the temperature reached a maximum of 135°C. After the reaction was 97% complete, the benzol was distilled off and the temperature went to 160°C.

However, analysis of the product indicated that there was still 10% benzene present. The contents were transferred to a two-liter beaker, placed in a steam bath, and a jet of air was passed over the surface for eight hours. A sample of this product had no loss in weight when placed in an oven at 110°C overnight. The product had a melting point of less than -10°C.

PREPARATION OF THE SODIUM SULFONATE OF 2-ETHYLHEXYL CINNAMATE

Using the procedure as described under the sulfonation of dodecylbenzene and shown in the sketch on Page 9, 2-ethylhexyl cinnamate was sulfonated. Seven hundred and eighty grams of the ester were weighed into the reaction vessel, and 480 grams (10% excess) of SO_3 were weighed into the SO_3 flask. The temperature of the reaction was maintained between 30 and 40°C. The SO_3 was added over a period of 30 minutes as a vapor diluted with air so that the SO_3-air ratio was 1-9. It was then allowed to remain in the acid for a total time of 60 minutes. The sulfonate was then added slowly to a beaker which contained a 50% solution of sodium hydroxide. The end product was a light brown paste. Control of the temperature of the reaction was very important. At higher temperatures, there was evidence of a breaking of the bond at the ester and forming the acid anhydride.

ANALYSIS OF THE SODIUM SULFONATE OF 2-ETHYLHEXYL CINNAMATE

Unsulfonated Oil	4.62%
Sodium sulfate	8.82%
Ash	19.1%

Evaluation of wetting properties (Method on Page .

1% solution at 25°C - 20 seconds
65% solution at 25°C - over 3 minutes

An attempt was made to determine the SO_3 content according to the method described on Page 113 of Analytical Methods for a Textile Laboratory by the American Association of Textile Chemists and Colorists. This method determines the sulfuric anhydride existing in a sulfated oil by boiling the sample with sulfuric acid and splitting off the organically-combined SO_3. Since the SO_3 would not split when this procedure was used on the above product, it is reasonable to assume that the hexavalent sulfur atom is linked directly to the carbon atom in the main chain.

From the analysis, there is evidence that this compound can be made and that the hexavalent sulfur atom is attached directly to the carbon atom.

The ash and sodium sulfate contents were high due to the fact that an excess of acid was used.

SULFONATION OF OLEIC ACID

Sulfonation of oleic acid with sulfuric acid has been known for many years, and the usual procedure for sulfonating is as follows: U. S. 1,923,608 (1933).

Oleic acid, 300 parts by weight, is mixed with 100 parts of acetic anhydride, and 300 parts of concentrated sulfuric acid is gradually added with stirring at about 0°C. After the mixture has become soluble in water, when checked by adding a few drops to a test tube of water, the excess of sulfuric acid is washed out with a solution of sodium sulfate. The resultant sulfonic acid is then neutralized to form the sodium salt.

Using SO_3 eliminated the need for acetic anhydride. However, on trials made by General Chemical Company, the product darkened considerably. Using the technique described on Pages 12 and 13, I made three runs sulfonating with SO_3 as follows:

> Four hundred and twenty-four grams of oleic acid purchased under the trade name "Olive Elaine" were placed in the SO_3 flask. The SO_3-air ratio was maintained at 1 to 9.5. The temperature of the reaction was held between 30 and 35°C. The time required for the addition of the acid was 60 minutes, and the sulfonate was left in the acid a total of 70 minutes. It was then neutralized with a 50% solution of sodium hydroxide. It was very important to add the sulfonate to the sodium hydroxide, because when added in reverse the product separated.

ANALYSIS OF THE SODIUM SULFONATE OF OLEIC ACID

Unsulfonated Oil	6.11%
Sodium sulfate	1.24%
Ash	2.20%
Color	Very light brown

An attempt was made to determine the SO_3 content according to the method described on Page 113 of Analytical Methods for a Textile Laboratory by the American Association of Textile Chemists and Colorists. This method determines the sulfuric anhydride existing in a sulfated oil by boiling the sample with sulfuric acid and splitting off the organically-combined SO_3. Since the SO_3 would not split when this procedure was used on the above product, it is reasonable to assume that the hexavalent sulfur atom is linked directly to the carbon atom in the main chain.

From the analysis, it appears that a higher ratio of acid to oleic acid should be used since the unsulfonated oil is high, and the ash and sodium sulfate are low.

The use of sulfur trioxide in sulfonating oleic acid has many advantages as follows:

1. Eliminates the need to use acetic anhydride in sulfonation.

2. Avoids the spent acid.

3. Reduces the ash and the sodium sulfate in the end product.

(Continued)

4. Oleic acid sulfonate made according to this method is resistant to sulfuric acid at 200°C.

SULFONATION OF PROPYLOLEATE

Sulfonation of propyloleate with sulfuric acid has been described, and the procedure for sulfonating is much the same as is used in sulfonating oleic acid. The propyloleate used was purchased from Sharples Inc., and the same technique as described on Pages 12 and 13 was used. Two runs were made as follows:

> One hundred and sixty-two grams of propyloleate were weighed into the reaction flask, and 80 grams of SO_3 were weighed into the SO_3 flask. The SO_3-air ratio was maintained at 1 to 9.5. The temperature of the reaction was controlled between 20 and 25°C. The time required for the addition of the acid was 75 minutes, and the total time in the acid was 150 minutes. The sodium sulfonate of propyloleate was added to a 50% solution of sodium hydroxide. As in the case of oleic acid, it was important to add the sulfonate to the sodium hydroxide.

ANALYSIS OF THE SODIUM SULFONATE OF PROPYLOLEATE

Unsulfonated Oil	3.72%
Sodium sulfate	2.34%
Ash	4.4%
Color	Light Brown

An attempt was made to determine the SO_3 content according to the method described on Page 113 of Analytical Methods for a Textile Laboratory by the American Association of Textile Chemists and Colorists. This method determines the sulfuric anhydride existing in a sulfated oil by boiling the sample with sulfuric acid and splitting off the organically-combined SO_3. Since the SO_3 would not split when this procedure was used on the above product, it is reasonable to assume that the hexavalent sulfur atom is linked directly to the carbon atom in the main chain.

From the analysis, it is evident that the sodium sulfonate of propyloleate can be made in good yield and color with the same advantages as in the case of oleic acid.

1. Makes it unnecessary to use acetic anhydride in the sulfonation.
2. Avoids the spent acid.
3. Reduces the ash and the sodium sulfate in the end product.

(Continued)

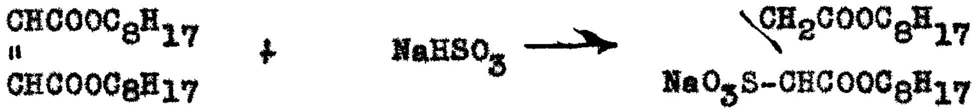
1. The sodium sulfonate of propyloleate made according to this method is resistant to sulfuric acid at 200°C.

PREPARATION OF DI-2-ETHYLHEXYL MALEATE

A three-neck, two-liter flask was set up with a water trap, condenser, agitator, and thermometer. Into the flask were weighed 98 grams of maleic acid and 260 grams of 2-ethylhexanol (equimolal ratio) with 160 grams benzol and 3 grams c.p. sulfuric acid. The mixture was heated over a bunsen burner with agitation until 17.5 cc of water were collected in a water trap. After the reaction was approximately 97% complete, the benzol was distilled off, and the temperature allowed to rise to 155°C. The contents were then transferred to a two-liter beaker and placed on a steam bath. A jet of air was passed over the surface for eight hours. A sample of this product had no loss in weight when placed in an oven at 110°C overnight.

SULFONATION OF DI-2-ETHYLHEXYL MALEATE

The sulfonation of Di-2-ethylhexyl maleate by addition of sodium bisulfite is very common and relatively inexpensive. It is marketed under the trade name, AEROSOL OT. The reaction may be shown as follows:



$$\begin{matrix} \mathrm{CHCOOC_8H_{17}} \\ \| \\ \mathrm{CHCOOC_8H_{17}} \end{matrix} + \mathrm{NaHSO_3} \longrightarrow \begin{matrix} \mathrm{CH_2COOC_8H_{17}} \\ \mathrm{NaO_3S\text{-}CHCOOC_8H_{17}} \end{matrix}$$

Using SO_3, attempts were made to sulfonate D-2-ethylhexyl maleate. Five hundred and ten grams of Di-2-ethylhexyl Maleate were added to the reaction flask, and 240 grams of SO_3 were added to the SO_3 flask. The ratio of acid to air was maintained at 1 to 9. The temperature of the reaction was maintained between 40 and 50°C. The time required for the addition of the SO_3 was 90 minutes, and the total time in the acid was 100 minutes. Four runs were made, and in all cases the percent SO_3 lost was between 30 and 50%. The ester apparently did not absorb the SO_3 very readily. The products were very dark, and large amounts of unsulfonated ester separated when the reaction product was added to sodium hydroxide. When 200 grams of the product were added to 200 grams of water, it separated into two phases. However, if the ester had been sulfonated, it would have been soluble in water. Backer and Vander Zander reported that excesses of SO_3 can be used to purify maleic anhydride (Chemical Abstracts 21-2, 1927). Their findings indicate that the SO_3 may have split the ester group and oxidized the product to maleic acid or maleic anhydride.

SUMMARY

The possibilities in the use of sulfur trioxide have by no means been exhausted, and it is hoped that some of the work carried out in this paper will stimulate others to investigate the reaction of other organic compounds with SO_3.

In summarizing this report, the following statements can be made:

1. The compounds listed below were sulfonated in good yield.
    a. Oleic acid
    b. Propyloleate
    c. 2-Ethylhexyl cinnamate
    d. Dodecylbenzene
2. Proper technique is important for good color and yield.
3. In the case of Alkylarylbenzenes, an octadecylbenzene does not sulfonate as well as a dodecylbenzene.
4. It was impossible to sulfonate Di-2-ethylhexyl maleate with sulfur trioxide.
5. Sulfur trioxide forms a sulfonated derivative in which the nexavalent sulfur atom is attached directly to a carbon atom.

BIBLIOGRAPHY

ALKANE - Oronite Chemical Company

SULFONATION - SULFATION -- E. E. Gilbert and E. P. Jones, Industrial and Engineering Chemistry, Volume 43, 1951

SULFONATION AND SULFATION -- E. E. Gilbert and E. P. Jones, Industrial and Engineering Chemistry, Volume 44, 1952

SULFONATION - SULFATION -- J. P. Sisley, American Dyestuff Reporter, Volume 43, No. 23, 1954

SULFONATION AND SULFATION WITH SULFUR TRIOXIDE -- Gilbert, Veldhuis, Carlson, Giolito, Industrial and Engineering Chemistry, Volume 45, 1953

SYNTHETIC DETERGENTS FROM ANIMAL FATS -- Stirton, Weil, Stawitzke, and James, Journal of American Oil Chemist Society, Volume 29, 1952

TECHNICAL SERVICE BULLETIN SF 1 -- General Chemical Company

TECHNICAL SERVICE BULLETIN SF 2 -- General Chemical Company

TECHNICAL SERVICE BULLETIN SF 3 -- General Chemical Company

UNIT PROCESSES IN ORGANIC SYNTHESIS - Groggins 3rd Edition, Mc Graw Hill