Sulfonation With Sulfur Trioxide[1]

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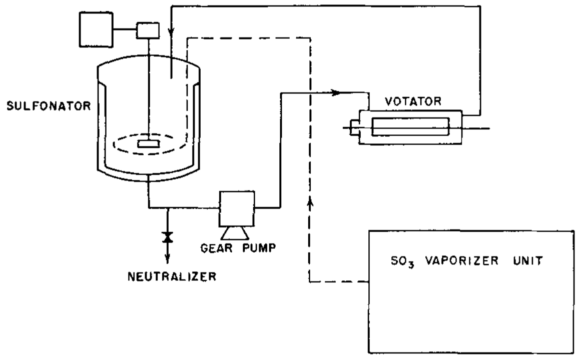
THE purpose of this paper is to present some of the more important factors encountered in the SO_3 sulfonation of alkylaryl hydrocarbons. This should serve as a basis for discussion and further study by those interested in the expanding field of alkylaryl sulfonate detergents.

The established method of producing this type of synthetic detergent has been to sulfonate with sulfuric acid. The strength of acid used may be from 98% to 20% free SO_3 oleum. Quantity of acid ranges from 1 to 1.5 pounds of acid per pound of alkylaryl hydrocarbon. The excess spent sulfuric acid is separated by a drowning procedure. The use of SO_3 as a sulfonating agent for the preparation of synthetic detergents is a relatively new art. It is practiced by only a few companies, but it is of rapidly increasing interest.

This paper will be limited to alkylaryl sulfonates of the type RSO_3M, where R is a 12-carbon alkyl substituted benzene and M is a metal or amine group. The alkyl group is a propylene polymerization product. The work was carried out in pilot scale equipment. Sufficient data were obtained to indicate the feasibility of the operation on a commercial scale.

Materials and Equipment

The dodecylbenzene used in this study is a product of Continental Oil Company, marketed under the name "Neolene 400." The SO_3 was obtained from vaporizing "Sulfan," a stabilized sulfuric anhydride manufactured by the General Chemical Division, Allied Chemical and Dye Corporation. This product is a water-white liquid, consisting of more than 99% SO_3, with minor amounts of sulfuric acid and stabilizing agent.



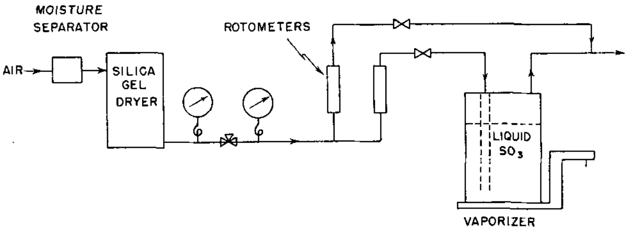
SULFONATION PILOT PLANT

——— REACTION MIXTURE
– – – – AIR – SO_3

FIG. 1.

The equipment used in this study (Figure 1) consisted of a sulfonation reactor, a vaporizer unit, a circulating pump, and a heat exchanger.

The sulfonation reactor was a jacketed 30-gallon Pfaudler glass-lined kettle, equipped with a 10-in. stainless steel turbine agitator. The agitator had a peripheral speed of 650 feet per minute. It was located two inches from the bottom of the kettle.



SO_3 VAPORIZER UNIT

FIG. 2

The SO_3 vaporizer unit (Figure 2), the property of the General Chemical Division, consisted of a silica gel air dryer, pressure and volume controls, and an electrically heated vaporizer. The air passed through a moisture separator and an air drier to a pressure-reducing valve. The air was then separated into two streams, each passing through a calibrated rotometer. The diluent air by-passed the vaporizer, joining the SO_3 stream before entering the sulfonator. The smaller air stream passed through the liquid SO_3 in the vaporizer, carrying SO_3 vapor to the sulfonator. The vaporizer was mounted on scales so that the rate of SO_3 addition could be measured. This SO_3-air stream was introduced to the sulfonator through four ⅛-in. holes in a ¼-in. O.D. stainless steel ring surrounding the agitator.

In the early work both reaction and cooling were carried out in the kettle itself. The heat transfer area provided by the jacket was inadequate to accomplish the necessary amount of cooling. For this reason dry ice was added directly to the sulfonation mass. Although impractical on a large scale, the results were sufficiently encouraging to warrant the development of suitable heat transfer equipment for the process.

Equipment which proved satisfactory was as follows. The material in the sulfonator was circulated by a 3-gal.-per-minute stainless steel gear pump, through a stainless steel laboratory Votator heat exchanger (a product of Girdler Corporation) and back into the sulfonator. The Votator heat exchanger was equipped with two blades which rotated on a shaft in the cooling chamber, scraping the heat transfer surface. It was driven by a 2-h.p. motor with a variable speed drive. Heat transfer area was 0.7 sq. ft.

All circulating lines and SO_3 vapor lines were of stainless steel. Temperature measurement of the sulfonation mass was done by a recording thermometer. Dial type thermometers were used to measure the temperature of the cooling water and the influent and effluent of the Votator heat exchanger. The cooling water rate was measured by a displacement meter.

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Procedure

The sulfonation was carried out by charging the dodecylbenzene to the kettle and agitating with cooling while adding the air-SO_3 stream to the mass.

One of the primary requisites of this process is to prevent any static contact of dodecylbenzene and SO_3. Such contact results in instantaneous charring and causes discoloration of the finished product. For this reason a small amount of air is always introduced through the SO_3 line in the kettle during the charging of dodecylbenzene. This is continued until the SO_3 flow is started, thus preventing dodecylbenzene from backing into the SO_3 delivery line.

It was found necessary to use a near maximum charge of dodecylbenzene in the kettle in order to get the greatest degree of sulfonation with a minimum of SO_3. A charge of 100-125 pounds was required to achieve the best results in this equipment. This effect was probably a function of height of liquid through which the gases were passing.

Experimental

Sulfonation temperatures from 45° to 80°C. were studied. Viscosities of the sulfonic acid were measured over a range of temperatures and at various times during the reaction. Colors of the finished sodium sulfonates were also obtained at the various sulfonation temperatures. Analyses were run to determine the degree of sulfonation. The final quantity of SO_3 added for all runs in this phase of the study was 110% of theory. Figure 3 shows the relationship of sulfonic acid viscosity and sulfonate color to sulfonation temperature. It can be seen that the viscosity rapidly decreases with increases in sulfonation temperature. From a processing standpoint it would be desirable to run at as high a temperature as possible. Color of the finished sulfonates began to darken rapidly however as sulfonation temperatures exceeded 55°C.; therefore, in order to achieve maximum quality at the lowest viscosity, a sulfonation temperature of 55°C. was considered optimum. Temperature had no noticeable effect on degree of sulfonation in the range studied. Sulfonate colors were obtained with a Klett-Summerson photoelectric colorimeter, employing a No. 42 blue filter. An 8.7% solution based on active material was used.

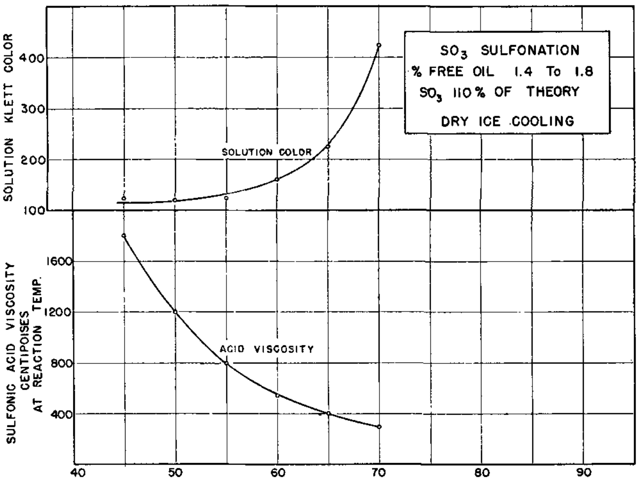

Fig. 3

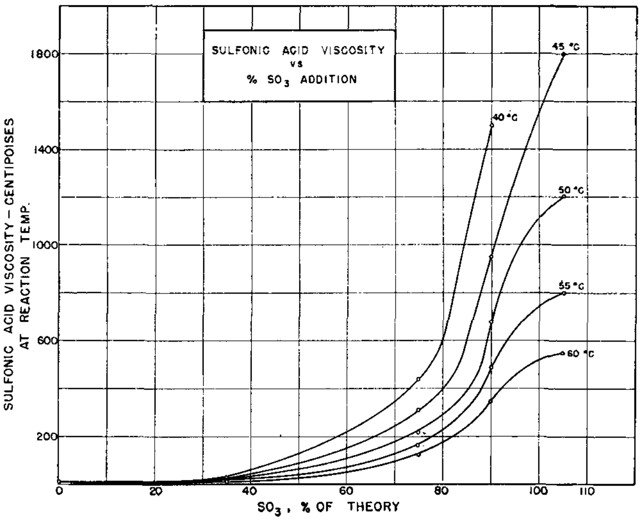

Fig. 4

Figure 4 shows that the high viscosity encountered occurs only after 75% of the required SO_3 has been added.

The quantity of SO_3 required to reduce the unsulfonated oil to less than 1.9% was slightly different, depending upon whether dry ice or external heat exchangers were used for cooling. With external cooling only 5 to 6% excess SO_3 over theory was required. With dry ice cooling 10% excess was required. One hundred per cent of theory is equivalent to 0.34 pound of SO_3 per pound of alkylate.

Volume ratios of air to SO_3 were also studied, and it was found that high volumes of air to SO_3 (at least 9:1) gave the best results in regard to sulfonate color and degree of sulfonation. Reduction of the air to SO_3 ratio resulted in significantly poorer colors and a decline in degree of sulfonation. It is believed that this poorer degree of sulfonation may have been the result of reducing the dispersion of the air-SO_3 input. Since all the work was done with the same size holes in the air-SO_3 delivery tube, any reduction of air velocity would result in a reduction in dispersion. It is possible that the optimum volume ratio may be different for other equipment.

In the equipment described about two hours were required to complete the SO_3 addition. It is desirable to carry out the reaction in a minimum of time followed by immediate neutralization of the sulfonic acid. When the time of contact with SO_3 was appreciably extended, the color of the finished sulfonate was dark.

In an effort to improve color further, a number of runs were made in which 97% sulfuric acid was added prior to the SO_3. This was added in an amount equivalent to 9% of the dodecylbenzene charge. The purpose of this "acid heel" was to reduce viscosity during sulfonation and thus obtain lighter colored sulfonates. This technique resulted in sulfonates of better color. No reduction of SO_3 requirement was realized. Analysis of this product showed the composition to be comparable to that of typical sulfonate prepared, using sulfuric acid for sulfonation.

Figure 5 shows the relationship of the degree of the sulfonation and of sulfonate color to the SO_3 in-

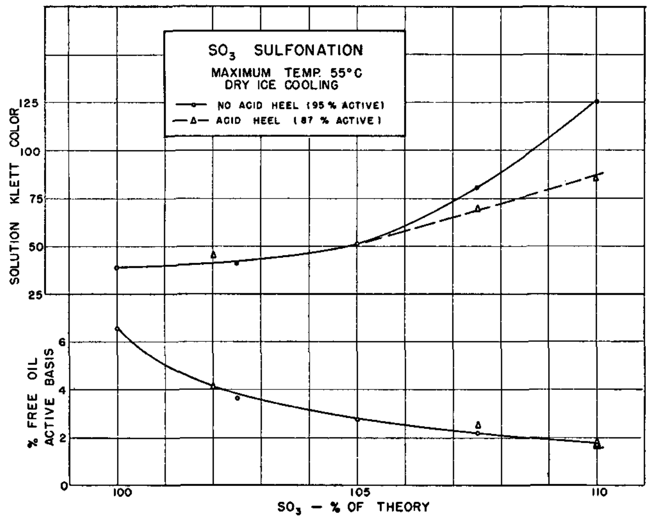

FIG. 5

put. The data on this chart were obtained using dry ice for cooling. A 10% excess of SO_3 over theory was required to reduce the free oil to a reasonable value (1.69%). Maximum activities obtainable approximate 95-95.5% on a solids basis when no acid heel is used or 87-87.5% when a 9% acid heel is used. Most of the color is picked up during the final stages of sulfonation. Although the excess SO_3 required was reduced to 106% with the advent of external cooling, no measurable quality change was noted.

Back pressure from the Votator heat exchanger was 75 p.s.i. during the viscous stage without an acid heel. This pressure drop was reduced to half when acid heel was used.

The over-all heat transfer coefficients determined on the Votator during this operation varied from 330 B.t.u. per hour per square foot per °F. during the initial stages of the sulfonation to slightly over 100 during the latter stage (Figure 6). The values were substantially the same with or without an acid heel.

Discussion

The heat of reaction of anhydrous SO_3 with dodecylbenzene is much higher than that of oleum (306 B.t.u. per pound of dodecylbenzene as compared with about 175 B.t.u. per pound (1, 2)]. The high viscosity of the sulfonation mass resulted in low heat transfer to the cooling medium in the kettle jacket. There is also present a smaller volume of reaction mixture per weight of alkylate when using SO_3. The combination of these factors results in a requirement for more efficient heat removal. The use of a Votator heat exchanger as an external heat exchanger on pilot scale batch sulfonation was very successful.

Long time of contact with SO_3 during sulfonation and low neutralization temperatures result in neutralized slurries which increase in acidity upon standing. For example, a slurry which has been neutralized to the basic side may develop a pH of less than 7. The free oil content of such a slurry immediately after neutralization is also higher than that of the same slurry after standing. These phenomena are believed to be due to the slow breakdown of anhydrides of the sulfonic acids present in the neutralized mass.

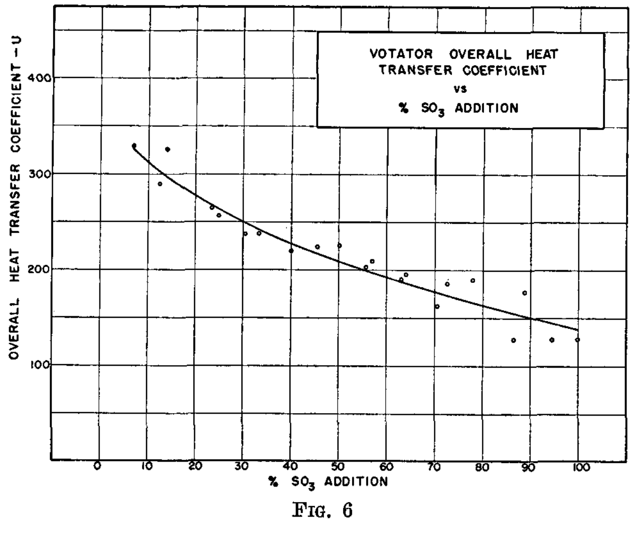

FIG. 6

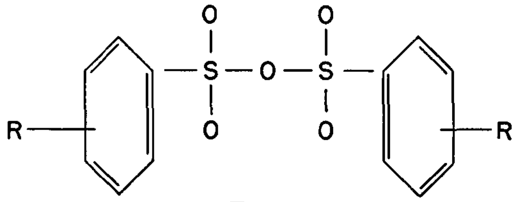

FIG. 7

These anhydrides would analyze as free oil immediately after neutralization. This explains the decrease in free oil content of the slurry. For each mole of anhydride formed, one mole of H_2O is probably produced. This water reacts with SO_3, yielding H_2SO_4 which ultimately appears as Na_2SO_4 in the neutralized slurry. The Na_2SO_4 content of the slurry is therefore proportional, to some extent at least, to the anhydride content and therefore to the acid drift to be anticipated. Indications have been obtained that rapid addition of sulfur trioxide during sulfonation and/or high temperature neutralization (70°C.) may alleviate this problem.

Dry air was used as the diluent gas for the SO_3 in all of the work reported in this paper. It is not necessary that the diluent be air; any dry inert gas or vapor may be used. It is also possible that the gas could be compressed and recirculated.

Summary

The results of this study indicate sulfonation with anhydrous SO_3 to be feasible. Heat removal is adequately accomplished with the Votator heat exchanger. Products are equivalent to or better than those from oleum sulfonation.

The relative values assigned to SO_3, sulfuric acid, and spent acid govern the economics of raw materials for this process as compared with using sulfuric acid. In most cases the sale price of the spent acid will be the controlling factor.

Following are several advantages and disadvantages of sulfonation with anhydrous SO_3.

Advantages

1. One of the foremost advantages is the elimination of handling, storing, and disposing of spent sulfuric acid. In some instances, this spent-acid problem has actually discouraged companies from entering the field.

2. The SO_3 type of sulfonation requires no aging or digestion period and no drowning steps to remove spent acid. This simplification results in a significant reduction in the time required to complete the operation. Depending upon the particular process and equipment used, this reduction can be as great as 60%.
3. The increased activity and lower salt content resulting from straight SO_3 sulfonation offer an obvious advantage to the manufacturer or potential manufacturer of liquid formulations. It has also been reported by some observers that the sulfonate odors are improved as a result of SO_3 sulfonation. Color of sulfonate is equal to that from oleum sulfonation.
4. Smaller volume equipment is required for a given quantity of alkylate.
5. The use of a higher sulfonation temperature than with oleum facilitates heat removal.

Disadvantages

1. The equipment required for the vaporization and handling of SO_3 is more extensive than that for handling oleum. This may be at least partially offset by reduction in equipment required for spent acid removal.
2. The high sulfonic acid viscosity necessitates more efficient heat transfer equipment.
3. The pH drift of the neutralized product from sulfonation without an acid heel might result in the requirement of a reneutralization step.

Acknowledgment

We thankfully acknowledge the cooperation of the General Chemical Division of Allied Chemical and Dye Corporation for their supporting laboratory data on this study.

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The Determination of Small Amounts of Trimethylene Glycol in High Gravity and Chemically Pure Glycerine

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IN 1919 Rojahn (1, 2) prepared tables for determining trimethylene glycol in high gravity and C. P. glycerines based upon the specific gravity and the water content. These tables are useful although it has long been recognized that they are slightly in error (3) due to the lack of sufficiently pure material and the shortcomings of the available methods. For this reason and because more exact data were available on the specific gravity of glycerol (4) and the more accurate Fischer volumetric method for water (5), it seemed appropriate to bring this phase of glycerine analysis up to date.

Analyses of sweet water concentrates have shown the presence of from 5 to 10% propylene glycol and 50 to 60% trimethylene glycol (6). These two compounds have very similar boiling points so that some propylene glycol will no doubt be present in high gravity and C. P. glycerine whenever trimethylene glycol is present. Refined glycerine usually does not contain a determinable amount of trimethylene glycol. Chemical methods like those of Pohle and Mehlenbacher (6) are satisfactory and generally applicable to samples containing more than 3% propylene and trimethylene glycols but cannot be considered suitable for smaller amounts. In the lower range the specific gravity and water methods must be employed.

The glycerol content of C. P. and high gravity glycerines can be determined most accurately by the specific gravity method (2) and somewhat less accurately from the water content determined by the Fischer volumetric method (5). When the sample contains only water and glycerol, 100 — % water equals the glycerol, and these results agree with the glycerol found by the specific gravity method. When the sample also contains trimethylene glycol, the percentage of glycerol found by the two methods does not agree, and the exact glycerol content is uncertain. Lawrie (3) gives a table for determining trimethylene glycol in high gravity glycerine from the specific gravity and water content of the sample. However it covers only the range of 0 to 3.0% trimethylene glycol when the water content varies between 0 and 2.5% so that the limited range for moisture will not include C. P. glycerines which contain approximately 5% water. Therefore a procedure was sought which would not require a table and could be applied to most of the conditions that are encountered in C. P. and high gravity glycerines.

The procedure which was investigated involved measuring the specific gravity at 25°/25°C. (8) and the water content by the Fischer volumetric method (5). Trimethylene glycol, including similar constituents, is calculated from these measurements and the change in specific gravity (0.0023) caused by a change of 1% in trimethylene glycol content. The factor (0.0023) was calculated from data in Lawrie's book (7) and was checked experimentally. The trimethylene glycol is calculated as follows:

A = % water by A.O.C.S. Fischer volumetric method (5)
B = specific gravity at 25°/25°C. by A.O.C.S. Method (8)
C = % glycerol from water content = 100-A
D = specific gravity at 25°/25°C. of a glycerol-water solution with a glycerol content of C.

Trimethylene glycol, %=(D-B)/0.0023=E

Glycerol, %=100−(A+E)

TABLE I

Properties and Composition of Compounds Used in Preparing Known Mixtures

Compound	Sp. gr. 25°/25° C.	Water, %	Trimethylene glycol, %	Propylene glycol, %	Glycerol, %
C. P. glycerin[a]	1.2492	4.9	0.0	0.0	95.0
High gravity glycerine (containing trimethylene glycol)[b]	1.2583	0.5	1.1	....	98.4
Trimethylene glycol (6)	1.0533	0.0	100.0	0.3	0.0
Propylene glycol (6)	1.0377	0.0	0.0	100.2	0.0

[a] Glycerol from specific gravity measurements.

[b] Trimethylene glycol and glycerol from method described above.