• Technical

Sulfonation with Sulfur Trioxide: Detergent Alkylate in a Scraping-Blade Heat Exchanger

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PREVIOUS WORK by the present authors, both on a laboratory and on a pilot-plant scale (2, 10), as well as by others (6, 12) has shown SO_3 vapor to be a practical sulfonating agent for dodecylbenzene detergent alkylate. This process has, in fact, been achieving increasing commercial acceptance over the past few years.

Although SO_3 is a more efficient reagent than oleum in several respects, it liberates considerably more heat of reaction, reacts more rapidly, and at the same time forms a more viscous reaction mixture (10). Despite the fact that these difficulties are not sufficiently serious to preclude the preparation of a satisfactory product in a simple reaction kettle that employs conventional agitation and cooling (2), it was felt that the evaluation of equipment especially designed for the efficient removal of heat from viscous materials would be of interest, especially from the standpoint of possible continuous operation. The so-called "high-speed scraping-blade heat exchanger," known as the Votator (16), fulfills these requirements. The Votator has, in fact, been described as producing "the highest known heat-transfer coefficients in the processing of high-consistency material" (15).

The results of a study of the sulfonation of dodecylbenzene with this equipment are reported herein as part of a program at this laboratory for developing uses for stabilized liquid SO_3, marketed by General Chemical Division under the trademark Sulfan (4).

The use of a Votator for the sulfonation of aromatic hydrocarbons is not new. Wilson (17) employed this equipment with a petroleum distillate, using sulfuric acid; he states that SO_3 vapor can also be used but gives no details. Continuous sulfonation of detergent alkylate with oleum in the Votator has also been described (11). Patents describe the use of vaporized SO_3 in the Votator to sulfonate detergent alkylate, higher molecular-weight alkylated benzene ("PDB"), and nonylnaphthalene (5, 13).

In the above-mentioned studies the reagents were mixed inside the Votator, which thus functions as a combined reactor and heat exchanger. This approach was followed in the present work. However other references (1, 6) cite the alternative procedure, not herein considered, of premixing the reagents in a separate vessel, followed by cooling in the Votator, which in these instances operates solely as a cooler.

Description of Equipment

The Votator comprises essentially an externally-cooled tube within which a shaft equipped with scraping blades rotates at high speed. The diameter of the shaft is three-quarters or more of the tube diameter, leaving only a narrow annular space through which the reactants pass rapidly and with turbulent agitation. The scraping blades continually remove the product film from the cooled tube, which results in exceptionally efficient heat-removal from the reaction zone. These basic features are shown in published drawings (12, 15, 16) and schematically in Figure 1. The Votator used in the present work was a laboratory model, with a tube 12 in. long x 3 in. in diameter.

Equipment layout employed in the present study is shown in Figure 1; a photographic view of this apparatus has been published previously (7). The equipment comprises three general sections: raw material feed system (including SO_3 vaporization), sulfonation section (in the Votator), and product collection.

Equipment Details (as numbered in Figure 1)

1. Sulfan supply, 100-lb. net drum, maintained at 30° to 35°C. by electric heating tape.
2. Sulfan Measuring Reservoir. Standard Pyrex pipe, 3 x 30 in. size. Machined steel-flanged ends, Teflon-gasketed, adapting to ½ in. pipe outlet to Sulfan pump. Reservoir was refilled at intervals from Sulfan supply. Delivered 0.50-lb. Sulfan per linear inch drop. Vented through small vessel of silica gel.
3. Sulfan Metering Pump. Milton Roy Minipump Model MMI-C-58-SM. Double-ball check pump with ⅛ in. diameter plunger. Fixed speed, variable stroke. Stainless 316 and Carpenter 20 construction. Teflon packing. Rated 1,800 cc. per hour. Temperature of pump and piping held at 30° to 35°C., controlled by electric heating tape of variable voltage.
4. Sulfan Vaporizer. Steel shell, 9 in. in diameter x 18 in. high, fabricated from welding caps and pipe section. All liquid and vapor connections through ½ in. stainless steel flexible hoses. Gas-heated. Placed on platform scale sensitive to 0.1 lb. Unit operated either as a batch or as a continuous flash vaporizer. Typical charge, 1 gal. of Sulfan.
5. Air Drier. Steel vessel, 12 x 30 in. high, packed with 75 lbs. of silica gel, which was regenerated at intervals with preheated air.
6. Air Flow Meters. Fischer and Porter Flowrater Rotometers, 1 to 20 cu. ft. per-minute range.
7. By-Pass Air Line.
8. Hydrocarbon Pump Tank. A 6-gal. steel drum on weigh scale.
9. Hydrocarbon Metering Pump. Zenith gear pump, stock unit Type B. Graham variable-speed drive. 0 to 60 lbs. per hour delivery, with 20 to 30 lbs. per hour standard.
10. Votator. Girdler Laboratory Model XIW. Functioned as combined reactor and heat exchanger; 3 in. in diameter x 12 in. of horizontal tube. Effective cooling-surface area, 0.68 sq. ft. Type 316 stainless steel construction. Interchangeable scraper shafts of varying diameter (see also Item 16). 2 h.p. drive through 4-speed gear box to give 260, 350, 580, and 1,080 shaft r.p.m., with normal procedures operated at 580 to 1,080 r.p.m. Shaft-supported at drive end by a ball bearing with a sealing gland of Teflon packing, and at free-end by sleeve-bearing of formed carbon. Air-SO_3 gas mixture introduced to shaft core and ports through carbon-bearing seal. Hydrocarbon introduced to Votator annulus *via* single ⅛-in. diameter port in end-plate.
11. Soaker Line. One in. stainless steel pipe, 3-ft. vertical rise, followed by 7-ft. horizontal run.
12. Receiving Tank. 5-gal. stainless steel vessel. Served as sulfonic acid receiver and as air-disengagement vessel.
13. Air Vent Line. Spent-dilution air discharged to atmosphere.
14. H_2SO_4 Heel Input Tee. Metered inlet from pressurized dropping funnel.
15. Votator Cooling System. Countercurrent flow at 4 gal. per minute by either full tap-water cooling or by water recirculation *via* a magnetic circulator pump (Teelpump,

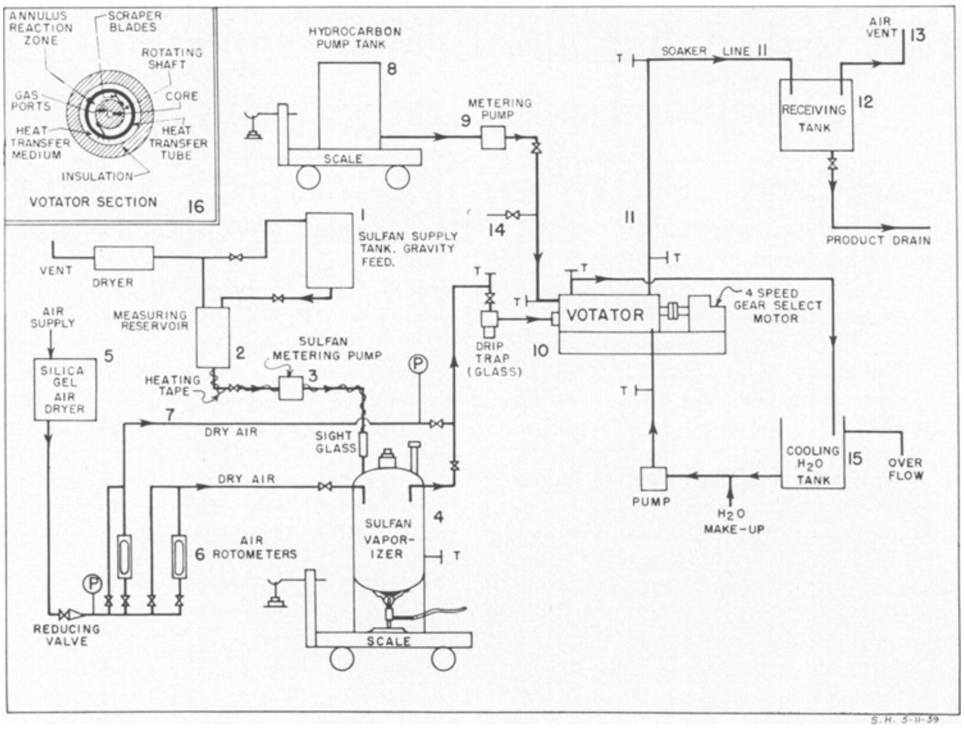

FIG. 1. Sulfonation pilot plant, using "Sulfan" in continuous "once-through" operation (see text for details of numbered items).

Model 300) from a 15-gal. steel drum reservoir to which make-up water was added as needed for temperature control.

16. Votator Shaft. (See also Item 10). Standard shaft was a 2⅞-in. in diameter cylinder, with two opposed metal blades fixed loosely on supporting pins and held in contact with the tube wall by centrifugal action. Air-SO_3 gas mixture was admitted through a carbon-bearing seal to the ⅜-in. in diameter core of the shaft, thence to the annulus reaction zone *via* 8 x ⅛-in. in diameter (or 3/32 in.) gas ports vertical to the core, with ports arranged regularly on a circumference circle located ¾ in. from the input-end of the shaft. To permit insertion of the shaft assembly into the 3-in.-in-diameter tube, the shaft was flattened slightly down its length along the planes of pin attachment.

Typical Operating Procedure

The alkylate is charged to the hydrocarbon pump tank (Item 8), and the measuring reservoir (Item 2) is loaded with Sulfan. The empty Sulfan vaporizer (Item 4) is next heated to 100°C. (± 20), and tap water (10 to 15°C.) is circulated through the Votator at 4 gal. per minute. Dry air (8 CFM) is admitted to the Votator *via* by-pass line (Item 7) and also (4 CFM) through the vaporizer. Alkylate is then continuously fed into the Votator *via* pump (Item 9) at a carefully measured and maintained rate of 0.400-lb.-per-minute. Sulfan is next introduced at 0.142-lb.-per-minute *via* the pump (Item 3) to the preheated vaporizer, where it is completely and continuously vaporized as indicated by constant scale-setting. The product sulfonic acid, still containing some unreacted hydrocarbon, is discharged continuously from the Votator to the soaker line (Item 11), where reaction is completed. The sulfonic acid collects in the receiving tank (Item 12). At this point diluent air is disengaged through the air vent line (Item 13). The reaction mixture is digested for 10 min., then mixed thoroughly for 5 min. with 1 to 1.5 weight % of water to eliminate anhydride.[1] The product is next withdrawn to storage or neutralization. Additional data are given in Table I.

Variables Affecting Product Quality

Two product quality-factors must be considered in preparing detergent alkylate sulfonate, most of which is used for household purposes: light color and low unreacted hydrocarbon ("free oil"). A third quality-factor, low inorganic sulfate content, is also of importance, especially in liquid formulations. Color values reported herein were obtained with the Klett-Summerson Photoelectric Colorimeter, Test Tube Model, using No. 42 blue filter on a 10% aqueous solution of the sodium sulfonate; the lower the number, the lighter the color. Products were tested immediately after preparation since light-fading occurs upon standing. A color value of 100 or less is believed satisfactory for all household uses. Sodium sulfate was determined by a standard analytical procedure (3). Free oil values should be below 1.5% by weight based on pure sodium sulfonate. Since the analytical procedure used for free oil is unpublished (14) and more convenient than the standard approach (3), details are given as follows:

Sodium sulfonate slurry (100 g., 40 to 45% active), ethylene glycol (30 ml.), water (150 ml.), two drops of "DC Antifoam B" or "DC 200," and boiling chips are charged to the apparatus shown in Figure 2. Further to inhibit foaming, a small lump of silicone stopcock grease is stuck on the inside of the flask near the top. Fill the side arm with water, and reflux for eight hours. Stop refluxing, and draw oil layer into narrow calibrated tube. Read ml. of oil.

$$\text{Percentage of free oil} = \frac{(\text{ml. oil})(0.88)(100)}{\text{activity}}$$

High oils can be estimated after 1 or 2 hrs., either by noting the size of the oil layer at the top or by draw-

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[1] Procedure subject of U. S. patent application Serial No. 480,068 (Continental Oil Company), and Canadian Patent 581,790 (Allied Chemical Corp.).

TABLE I

Typical Preferred Operating Data (2⅞-In. Shaft)

Factor	Value
Alkylate reacted (lbs. per hr.)	24
SO_3 vaporized and reacted (lbs. per hr.)[a]	8.5
Diluent air (total CFM)[b]	12
Water coolant temp. (°C. at inlet)	10–15
Operating temp. (°C. at Votator outlet)	38–42
Votator RPM	1080
Digestion time (min.)	10
Water treatment	
Wt. % on product	1–1.5
Reaction time (min.)	5
Production rate (lbs. sulfonic acid per hr.)[c]	32.3
Product color [d]	75–100
Free oil in product [d]	0.5–1.25
Sodium sulfate in product [e]	3–4

[a] At 110% of theoretical mole ratio.
[b] 67% by-passed; 95% over-all air dilution.
[c] Weight percentage, based on pure sulfonate.
[d] See text for significance of color and free oil values.
[e] Weight percentage based on pure sulfonate.

ing it down into the constricted section and returning it to the system with the associated water. Foaming may become excessive toward the end of the heating period; this can be controlled by reducing the heat or increasing the size of the flask. Lauryl sulfate can be analyzed similarly using a 24-hr. heating period.

Shaft Design. A high ratio of shaft diameter to enclosing tube is by far the most important single apparatus design factor affecting product quality and operation. A 1¼-in. shaft in the 3-in. tube gave an inferior product, probably because of poor mixing. The 2¼- and 2⅝-in. shafts gave optimum colors at best in the range of 125–200. The 2⅞-in. shaft, on the contrary, not only gave the products of best quality (*i.e.,* color 75–100) but differed radically in performance from those of lesser diameter. It showed marked sensitivity, respecting product quality, to variations in shaft speed not shown by the others. It advantageously permitted operation at a lower temperature, was considerably more efficient in the removal of heat, and responded differently to variations in air dilution. In addition, about 99% of the reaction occurred in the Votator proper as opposed to about 95% when using smaller shafts. Calculation showed that, with the 3-in. enclosing tube, the 2⅞-in. shaft has about one-third to one-fourth the reaction space of the 2⅝-in. shaft. Gas-retention time for the larger shaft is estimated at less than 0.025 of a second, emphasizing that most of the reaction proceeds nearly instantaneously. This suggests that a critical degree of intense mixing, which is promoted by the smaller reaction space around the large diameter shaft, is more essential to complete and efficient sulfonation than the longer retention-time of the smaller shaft.

Several other shaft designs, all 2⅝ in. or less in diameter, were tested to no advantage. These included aeration shaft (gas fed close to cooling wall *via* projecting pins); liquid injection shaft (alkylate injected *via* center of shaft; sulfur trioxide added *via* port in end-plate); four-bladed shaft (as opposed to two blades). A spiral shaft (no mechanical contact with wall, imparts pumping action) was likewise of no special value.

Scraper-shaft diameters greater than 2⅞ in. were not tested. Further improvement might conceivably result although increase in back pressure might present an operating problem. With the 2⅞-in. shaft the pressure was low and presented no difficulty.

Position and size of the gas-feed ports in the 2¼-in. shaft were varied as follows: a) concentration at input-end of shaft (standard procedure); b) in parallel rows extending down the first 60% of the shaft input-end; rows varied in number and position relative to shaft blades; c) number and size varied from 2 x ⅛ in. in diameter, to 8 x ⅛ in., to 26 x $\frac{1}{16}$ in., etc.; d) output-ends of ports flush with shaft surface *vs.* closeness to wall of cooling surface *via* projecting pins. (Gas feed *via* the Votator end-plate, as opposed to the shaft, is discussed separately below.) It was concluded that none of these variations, as well as one cited in a patent (13) as preferred, markedly affect product quality.

Metal and plastic scraper-blades, mounted either freely "floating" or spring-loaded, were tested. Spring-loading gave excessive wear. Plastic (glass, Teflon) blades showed slightly poorer heat-transfer than metal. Operation under optimum conditions with the blades removed gave a product of very poor color in spite of the vigorous agitation induced by the supporting pins. The importance of the scraping action of the blades was thereby directly demonstrated.

Shaft Speed, Air Dilution. The data plotted in Figure 3 show that an air dilution of 95% at 1,080 r.p.m. gives optimum product color with the 2⅞-in. shaft. Contrary to results noted with shafts of smaller diameter, greater air dilution did not effect a corresponding improvement. These results suggest that shaft speeds higher than the maximum 1,080 r.p.m. attainable in the present study might give even lighter colors.

Alkylate Quality, Reactant Ratio. Two commercial detergent alkylates were used in this study. With the 2⅞-in. shaft, both gave product colors below 100, even with 117% of theoretical sulfur trioxide. With Alkylate II, free oil values could be progressively lowered from 1.0% (at 109%) to 0.2% (at 117%).

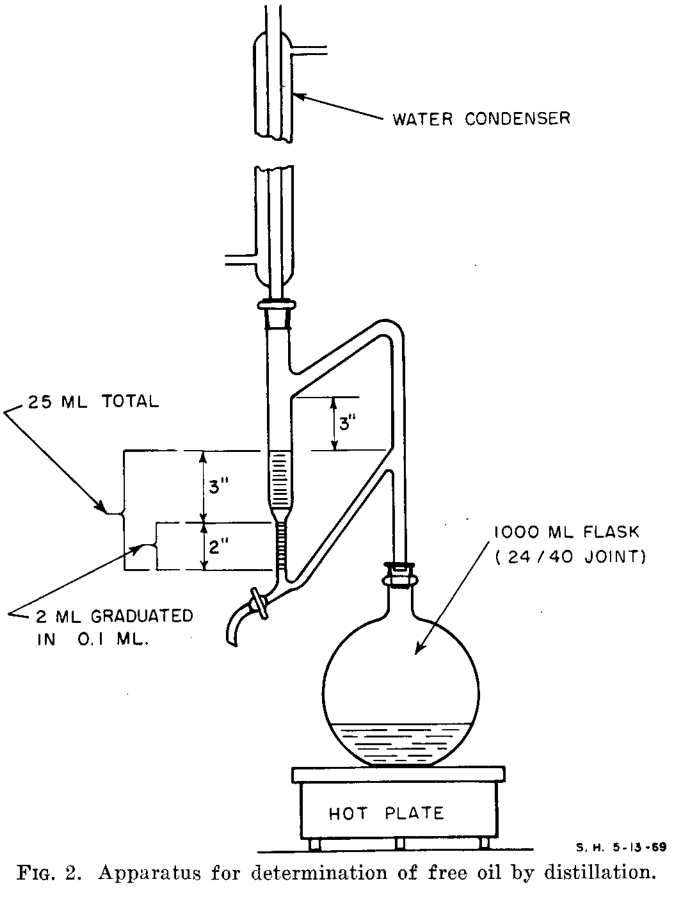

Fig. 2. Apparatus for determination of free oil by distillation.

With Alkylate I, 0.7% was the minimum free oil attainable, indicating the presence of an unsulfonatable constituent. Also, as shown in Figure 3, Alkylate II gives somewhat lighter products than Alkylate I under comparable conditions.

Product color darkens with increasing SO_3-to-hydrocarbon ratio. With the $2\frac{5}{8}$-in. shaft there is a break-point at about 105%, below which darkening is gradual but above which it increases rapidly. With the $2\frac{7}{8}$-in. shaft, on the other hand, the break-point is above 115%, and the rate of increase below that point is more gradual than with the smaller shaft.

Reaction Temperature. Lowering the reaction temperature (*i.e.,* at Votator outlet) over the range 50 to 28°C. lightened product color from 1 to 2 Klett points per degree, with the $2\frac{7}{8}$-in. shaft. The range 35–45°C. was accordingly chosen for practical operation because it gave good color without requiring refrigerated coolant. Smaller shafts, on the other hand, could not be used below about 50°C. without serious darkening of product.

Feed Rate. Product colors remained substantially unchanged over the range 15 to 25 lbs. of alkylate feed per hour. The latter is the maximum rate attainable with available equipment.

Use of Soaker Line. A small proportion of the reaction occurs in the soaker line, thereby desirably reducing the free oil without loss of color. With the $2\frac{5}{8}$-in. shaft, oil values were 5, 3, 1.5, and 1.5% at total lengths of 0, 3, 10, and 22 feet; packing did not increase efficiency. Since some heat was evolved, the soaker line was jacketed and water-cooled for the first three feet. Corresponding oil values for the $2\frac{7}{8}$-in. shaft at lengths of 0 and 10 ft. were 1.5 and 1.0%; for this minor degree of reaction, external cooling of the line proved unnecessary.

Use of "Heel." This term designates the addition of sulfuric acid (up to about 10% by weight on the hydrocarbon) before sulfonation with sulfur trioxide vapor (8); viscosity of the reaction mixture is thereby reduced and a light-colored product usually results but at the expense of a correspondingly higher content of sodium sulfate. Using the $2\frac{7}{8}$-in. shaft, neither alkylate gave lighter colors with a heel. On the other hand, smaller shafts did yield substantially lighter products (*i.e.,* below 100) by this procedure. It may be conjectured that the greater excess of sulfur trioxide (110%) used with the large shaft, as opposed to that (105%) used with the smaller, may in effect be performing the function of a heel.

Digestion and Anhydride Removal. To achieve minimum free oil without substantial loss of color, the sulfonic acid is digested for about 10 min. Digestion for a longer period leads to darker color without further reduction of oil. Sulfonates prepared with sulfur trioxide must be processed to remove sulfonic acid anhydride (9). A statement in the literature (13) to the effect that anhydride is not formed during sulfonation of detergent alkylate with sulfur trioxide in the Votator is concluded to be incorrect on the basis of the present work. If anhydride is removed by adding water, neutralization should follow promptly for best color. During the first 4 hrs. after water treatment, the sulfonic acid will lose as much as 30 color points. Darkening is much slower thereafter.

Method of Introducing Sulfur Trioxide. Although in the present study the alkylate was introduced through a single port near the circumference of the end-plate of the Votator, and the sulfur trixode through holes in the shaft, it would be decidedly preferable, for design reasons, to introduce both materials through the end-plate on a commercial scale. It was found that location of the gas port at the top of the end-plate, with the alkylate port opposite at the bottom, gave results at least as good as by the usual procedure. However reversal of the positions of the ports gave poor results. It was conjectured that premature inefficient mixing may have occurred in the $\frac{3}{8}$-in. "dead" space between the end-plate and the shaft, when the liquid was introduced at the top. Reduction of the volume of the dead space was, in fact, found to improve product quality somewhat. Selection of the correct point of introduction of sulfur trioxide therefore appears essential for best product quality.

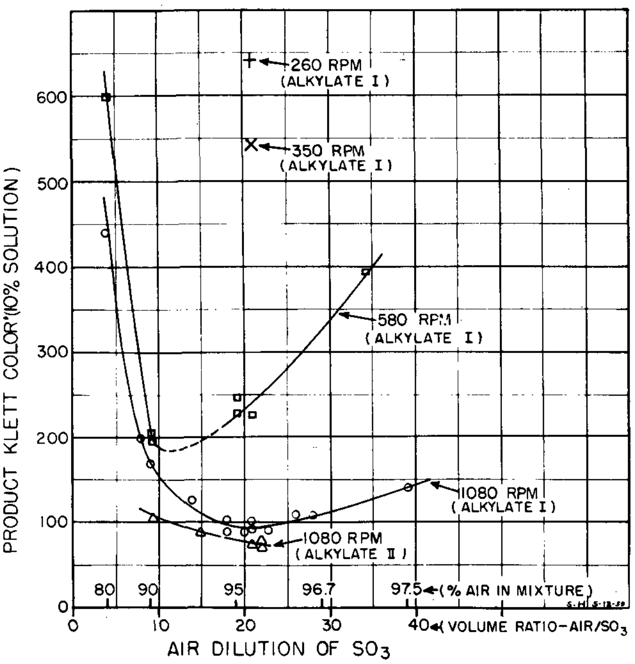

FIG. 3. Effect of air dilution upon product color at various shaft speeds (once-through sulfonation, using $2\frac{7}{8}$-in. shaft).

Attempts to apply the sulfur trioxide directly in liquid form without vaporization were not promising since free oil and color values were very high, indicating extensive degradation by de-alkylation. On the other hand, when employing it in the vapor form, even when using a large excess leading to dark color, the oil values were acceptably low, indicating lack of deep-seated decomposition. These results are consistent with previous observations (10) by the present authors.

"Once-Through" vs. "Cyclic" Operation. The present process operates on a "once-through" basis. By installation of a circulating pump and an extra tank, the Votator was also tested in "cyclic" operation. This involved recirculation of a given batch of alkylate through the Votator until sulfonation was complete. Such a process could be operated commercially with continuous vaporization and sulfonation in conjunction with two recycle tanks equipped for immediate change-over to allow their alternate use. Because of much higher liquid-to-gas ratio in the cyclic approach, entailing higher back-pressure, it

could not be used with the 2⅞-in. shaft. With smaller shafts however it showed promise, yielding products with acceptable colors and oils. In fact, the colors were considerably lighter than those noted with the same shafts on a once-through basis and about equal to those obtained in the present process. Because of the limitation of back pressure, productivity of the cyclic process was only about half that of the other. However this difficulty can probably be overcome, at least partially, by using higher pressure for the diluent air or by installing auxiliary piping of larger diameter. As discussed more fully in a subsequent section, the cyclic method is potentially even more productive based on capacity for heat removal. It is therefore felt that the cyclic procedure could be a preferred commercial approach under some circumstances although in general it appears more cumbersome than once-through operation.

Relatively minor equipment changes in the cyclic process permitted evaluation of the "dominant bath" principle. This procedure, widely used industrially for sulfonating detergent alkylate with oleum, employs the circulating reaction mixture as the reaction medium; the finished product is obtained by continuous bleed-off from the circulating stream. In the present work the sulfonic acid was recirculated at rates varying from 5 to 20 lbs. per minute, with fresh alkylate being introduced at 0.4 lb. per minute prior to entry into the Votator. The corresponding vaporized sulfur trioxide was added somewhat downstream from the hydrocarbon by the usual procedure through the Votator shaft. In all cases, product quality was decidedly unacceptable. It was concluded that repeated exposure of the sulfonic acid to sulfur trioxide results in degradation whereas such does not occur with the milder reagent, oleum. This conclusion was substantiated by greatly reducing the rate of recirculation of the sulfonic acid to 0.1 lb. per minute while holding constant the rates of addition of alkylate and sulfur trioxide. Product quality was much improved but still unacceptable.

Variables Affecting Heat Transfer

Since sulfonation with sulfur trioxide is a highly exothermic (10), virtually instantaneous reaction, efficient heat removal is of prime interest both for high productivity and for good product-quality. It therefore appeared of interest to explore the operational factors governing the efficiency of heat exchange (U) since the Votator is specifically designed for this purpose.

Values of U were calculated by measurement of heat absorption by the cooling water. For a typical run made under the conditions summarized in Table I, U is calculated as follows:

$$U(\text{BTU/hr./sq. ft./}^\circ\text{F.}) = Q_{(H_2O)}/\text{Cooling Area})(\triangle T_{(^\circ F.)})$$

$Q_{(H_2O)}$, heat absorbed by coolant, as BTU/hr., is 8200 based on:

Pumping rate (lbs. water/min.) : 23.8
Temperature water (out −°C.) : 14.7
Temperature water (in −°C.) : 11.5
Temperature rise (°C.) : 3.2
Average water temperature (°C.) : 13.1
$\therefore Q_{(H_2O)} = (23.8)(3.2)(1.8)(60) = 8200$
Cooling area of Votator (sq. ft.) = 0.68

$\triangle T_{(^\circ F.)}$ (difference between average temperatures of reaction mixture and coolant) is 48.5, based on:

Temperature of reaction mixture (°C.) : 40.0
Temperature of water (°C.) : 13.1
Difference $(\triangle T_{(^\circ C.)})$: 26.9
$\therefore \triangle T_{(^\circ F.)} = (26.9)(1.8) = 48.5$
U is therefore : $8200/(0.68)(48.5) = 250$

The data in Table II were obtained similarly. All values of U are approximate since it was only possible to measure the temperature of the reaction mixture at the outlet of the Votator rather than preferably to take the integral heat over the entire reaction area.

TABLE II

U *vs.* Air Dilution,
Shaft Speed and Feed Rate (2⅞-in. Shaft)

Percentage air	Values of U			
	580 RPM	1080 RPM		
	Feed rate [a] 0.25	Feed Rate [a] 0.25	Feed Rate [a] 0.35	Feed Rate [a] 0.40
78.8	......	235	......	......
80.0	270	......	......	......
89.2	......	245	......	......
90.1	270	......	......	......
93.3	......	250	......	......
93.8	......	......	......	270
94.8	......	225	265	255
95.0	180	......	......	......
95.3	......	......	......	250
95.5 [b]	135	220	......	......
95.8	......	......	235	......
96.2	......	210	......	......
96.5	96	......	210	......
97.5	71	175	......	......

[a] Pounds alkylate per minute.
[b] U = 25, 40, 55 at 0, 260, 350 r.p.m. (feed rate 0.25 to 0.30 lb. per min.).

In the range of 94.8 to 97.5% air-dilution, the value of U decreases with increasing dilution but increases with greater shaft speed. Both of these results accord with expectation, corresponding to poorer heat-tranfer through a gas and better transfer with more intense agitation. It is not apparent why the value of U (for 1080 r.p.m. and a feed rate of 0.25) should decline at air dilutions less than 93.3%.

Once-through operation with smaller shafts gave U values in the range 77 to 135 under optimum operating-conditions, indicating much less efficient heat removal than obtained with the 2⅞-in. shaft. This difference is considered a probable major reason for the substantially darker product colors obtained with smaller shafts. Regardless of shaft size, shaft speed and degree of air dilution are the major factors affecting the value of U in once-through operation, with feed rate and reaction temperature having minor influence.

It is interesting to note that products of excellent color were obtained, both in the laboratory (10) and in the pilot plant (2), using the kettle type of batch reactors of comparatively low heat exchange efficiency (over-all U = 28). Batch operation differs basically from once-through in that sulfur trioxide is added slowly to the total hydrocarbon in the former approach while in the latter both reagents are mixed all at once in stochiometric proportions. Batch operation therefore in effect entails use of a diluting solvent, which at first is unreacted hydrocarbon and toward the end is the reaction product; such is not the case with the once-through procedure. Efficient heat removal is consequently less crucial for the best product color in batch operation.

Cyclic operation in the Votator with a small shaft is chemically similar to batch operation as described above, and it produces products of equally good quality. The fact that it gave U values in the range of 200 to 250 is considered of minor influence. However it does lead to the conclusion that, if a Votator with a small shaft is to be used for continuous sulfonation, cyclic operation is preferred over once-through both for quality and efficiency of heat removal even though it may be somewhat less straightforward mechanically, as discussed above.

Summary and Conclusions

Two continuous processes for sulfonating detergent alkylate with sulfur trioxide vapor have been developed by using a Votator high-speed, scraping-blade heat-exchanger. Both procedures yield products suitable for household use without bleaching.

For the process of major interest, involving once-through operation, the ratio of shaft diameter to the enclosing shell is the prime factor governing equipment performance and product quality. This factor is not critical for the second method, involving cyclic operation. Numerous other process variables were studied for both procedures, with special emphasis on how they affect product quality and efficiency of heat transfer.

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Improved Process for the Preparation of Conjugated Soybean and Lower Alkyl Vinyl Ether Copolymers by Flash Polymerization[1]

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DURING THE PAST YEAR an extensive research program has been in progress at this laboratory on the preparation and evaluation of new vinyl ether monomers derived from soybean and linseed oils. Pure vinyl ethers capable of polymerization were produced without significant loss of unsaturation by reacting fatty alcohols with acetylene at atmospheric pressure (1, 2). Copolymerization of the fatty vinyl ethers with various comonomers was accomplished at room temperature by using Lewis-acid-type of catalysts and a flash technique in solvent (5). Baked copolymers dried to hard varnish-like films that had good resistance to acids, alkalies, and solvents. Among the comonomers studied, the lower alkyl vinyl ethers appeared most promising for baked metal and can coatings (4, 5, 6, 8).

From the view-point of economics and performance isobutyl and ethyl vinyl ethers were selected for more intensive industrial evaluation. The test samples were prepared both on a laboratory and pilot-plant scale. Isobutyl, ethyl, and n-butyl vinyl ethers were copolymerized by flash techniques with conjugated soybean vinyl ether at a mole ratio of 3:1 lower alkyl/fatty monomer, using stannic chloride catalyst in solvent. Improved techniques of polymerization and catalyst handling are reported from the standpoint of commercial process development. A simplified procedure for separation of catalyst, using hydrated lime, is described; turbo-agitation is proposed as a method for obtaining essentially water-white copolymers; and two solvent recovery processes are described.

Experimental

Materials and Equipment. Fatty vinyl ether monomers were prepared by atmospheric vinylation of conjugated soybean fatty alcohol in the presence of

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