require the planting of about 65,000 acres and result in a gross income of about $5 million.

Acknowledgment

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Laboratory Sulfonation Methods for Detergent Alkylbenzenes

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Abstract

Laboratory methods are described for evaluation of alkylbenzenes by three different sulfonation techniques: batch oleum sulfonation, continuous oleum sulfonation, and batch sulfur trioxide-air sulfonation. Sulfonation conditions such as temp, mixing, and reaction time are carefully controlled; and the resulting sulfonates are reproducible in quality. Of particular interest is the close control of the sulfonating agent feed rate. In the batch oleum method, this is accomplished by flow through a calibrated capillary under constant head and in the SO_3-air method, by constant rate injection of liquid SO_3 into the vaporizer. In the continuous oleum method, both alkylate and oleum feed rates are kept at desired levels with a duplex positive displacement pump which pumps against spring-loaded ball check valves in the lines to the mixing pump.

Sulfonation data (including solution colors and unsulfonated oil contents of the products) are presented for several commercial detergent alkylbenzenes varying in average mol wt from 241–267. Quality of the alkylbenzene is more critical for the continuous oleum and batch SO_3-air methods than for the batch oleum sulfonation.

Introduction

SINCE THE INTRODUCTION of detergent alkylbenzene sulfonates after World War II, their use has steadily grown to a present level of about 600 M lb/year (10); and they now comprise the largest single type of detergent active production. As their usage increased, improvements in the quality of the detergent alkylbenzenes were continually made to meet the exacting quality standards required by the detergent manufacturers and formulators.

Two of the most important sulfonate quality inspections which concern the detergent manufacturer are unsulfonated oil content and color. Lower unsulfonated oil content means greater sulfonate yield and often better odor and foam performance. Color has become increasingly important because of the consumers' preference for light colored products. Low sulfonate color means savings through reduced requirements in bleaching or in matching uniform colors in dyed products.

Not only the quality of the alkylbenzene but also the method of sulfonation affect the unsulfonated oil and color of the sulfonate. Furthermore, the same alkylbenzene may give a good quality product by one sulfonation procedure but a poor product by another method. Thus, it is imperative that rapid and meaningful laboratory sulfonation tests be available to evaluate detergent alkylbenzenes. This paper presents three laboratory sulfonation methods: batch and continuous oleum sulfonation and batch SO_3-air sulfonation. These methods have proven useful in evaluating differences in alkylbenzenes as well as in developing new alkylbenzenes of the highest quality.

The conditions and reactant ratios given in the methods are those normally used for laboratory evaluations of detergent alkylbenzenes. However, the procedures offer great flexibility as regards temp, reaction times, reactant ratios, and mixing. Usually, the sodium alkylbenzene sulfonates are prepared; but preparation of other salts, such as ammonium or potassium, is equally feasible.

Batch Oleum Sulfonation

Experimental Procedure. Details of the batch sulfonation reactor are shown in Figure 1. Other equipment necessary includes an ice bath, a hot water bath at 180–190F, and two constant temp baths at 120F and at 150F, respectively. The heating or cooling water is circulated through the reactor jacket with a centrifugal pump. Temp, times, and stirring rates are precisely controlled; while the rate of addition of the oleum, which is of particular importance, is maintained by flow through a replaceable calibrated capillary tube under a const head. After completion of the sulfonation step, the reaction mixture is diluted with water to facilitate phase separation of spent acid and sulfonic acid.

Alkylbenzene (1.4 moles) is charged to the reactor and cooled to 40–45F by pumping ice water through the reactor jacket and stirring the alkylbenzene at 900 rpm. Twenty-two per cent oleum (4.5 moles of equivalent SO_3; 3.2/1.0 mole ratio of sulfonating agent/alkylbenzene) is charged to the dropping funnel, the stopcock is opened wide, and the glass stopper is momentarily loosened until oleum covers the delivery tube of the dropping funnel. Oleum will now drop into the sulfonator through the capillary tube under const head and therefore at a const rate. Using a ½-inch long, 1-mm ID capillary tube, the addition

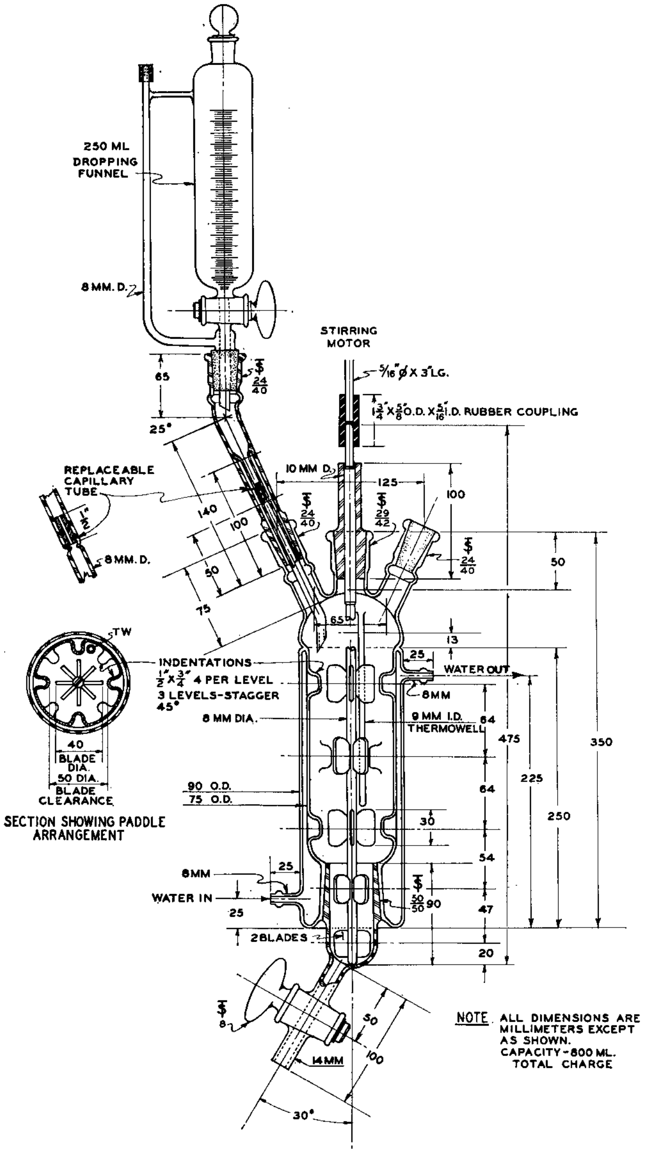

FIG. 1. Batch oleum sulfonation reactor.

rate is 7.3–7.8 ml/min. The oleum delivery is adjusted so that the oleum drips directly into the alkylbenzene. Five min before the end of oleum addition, circulation of cooling water is stopped, allowing the reaction mixture to warm to 75–80F. When all the oleum has been added, water at 180–190F is pumped through the sulfonator jacket until the temp of the reaction mixture is 85F. The hot water circulation is then stopped, and the temp of the reaction mixture will rise to approx 120F. Stirring is continued for 1 hr while the reaction temp is maintained at 118–122F by pumping 120F water from a const temp bath through the heating jacket.

At the end of the digestion period, water (77 ml) is added from the dropping funnel over a period of 5–6 min while the temp of the reaction mixture is kept below 140F by circulating ice water. About 1 min before the end of the water addition, water at 180–190F is pumped through the sulfonator jacket until the reaction temp has risen to 145F. The 180–190F hot water is stopped, and the reaction temp will coast to 150–155F. The stirring is stopped, and the spent acid is allowed to settle for 60 min. During the spent acid settling, the reaction temp is maintained at 150–155F by circulating 150–155F water through the sulfonator jacket. Upon completion of the phase separation, the spent acid (bottom layer, 79% sulfuric acid strength) is drained from the reactor and discarded.

The sulfonic acid (top layer) is emptied into a 1-liter dropping funnel and neutralized by adding it slowly to 450 ml of 12.4% aqueous sodium hydroxide solution cooled in an ice-water bath and stirred with an Eppenbach mixer (Model L-1, Gifford-Wood Co.). The slurry temp is maintained below 110 F to avoid gel formation. After adding approx 350 ml of sulfonic acid, the pH of the slurry is checked periodically, using a spot plate and Grammercy Universal Indicator. Acid addition is stopped when the slurry pH is between 7.0 and 7.5. The resulting slurry contains 38–42% sodium alkylbenzenesulfonate and 5–7% sodium sulfate.

Discussion of Procedure. The procedure given in the experimental section is that normally used for detergent alkylbenzene evaluation because experience has shown that such conditions usually distinguish clearly between alkylbenzenes of varying quality (unsulfonated oil content and color). However, a wide variety of experimental conditions can be used in the method. Acid addition rates are easily varied from 30–120 min by using capillaries of different lengths, and other reaction conditions are even more easily changed. Of course, decreasing the temp, the oleum/alkylbenzene ratio, the oleum strength, or the digestion time normally decreases the sulfonate color and increases the oil content and *vice versa.* Detailed data on these variables have been reported previously in the literature (8,9), and similar qualitative correlations are found for this batch oleum sulfonation procedure.

Continuous Oleum Sulfonation

Experimental Procedure. Details of the continuous oleum sulfonation equipment are given with the schematic drawing of the unit in Figure 2.

Precise control of the oleum and alkylbenzene feed rates is maintained by pumping through spring-loaded ball check valves into the suction side of a centrifugal pump. The oleum line extends to within about 1.5 mm of the pump impeller to assure fast mixing. Heat of reaction is removed by recirculation of the reaction products through a water-cooled glass heat exchanger. The overflow from the top of the heat exchanger is heated to the desired digestion temp in another heat exchanger and then passed through three digestors surrounded by a const temp bath.

Total feed rate of oleum plus alkylbenzene is standardized at 20 ± 0.5 ml/min, 20% oleum is used, and the temp at the discharge of the mixing pump is maintained at 118–120F. Recirculation rate is 300–400 ml/min, digestion temp is 120F, and digestion time is 28 min. While feed rates and sulfonation temp are being established at const values and for about 30 min thereafter, reaction products are collected ahead of the digestors and discarded. After this, reaction products passing through the digestors are discarded for another 5 min before a sample is taken for product evaluation. The whole acid is neutralized immediately as it leaves the last digestor by adding it to 12.4% sodium hydroxide solution agitated with a glass stirrer and cooled in an ice bath. The resulting slurry contains about 14–17% sodium alkylbenzenesulfonate and 13–15% sodium sulfate. If it is desired to evaluate the effect of digestion time on sulfonate quality, samples may be taken ahead of

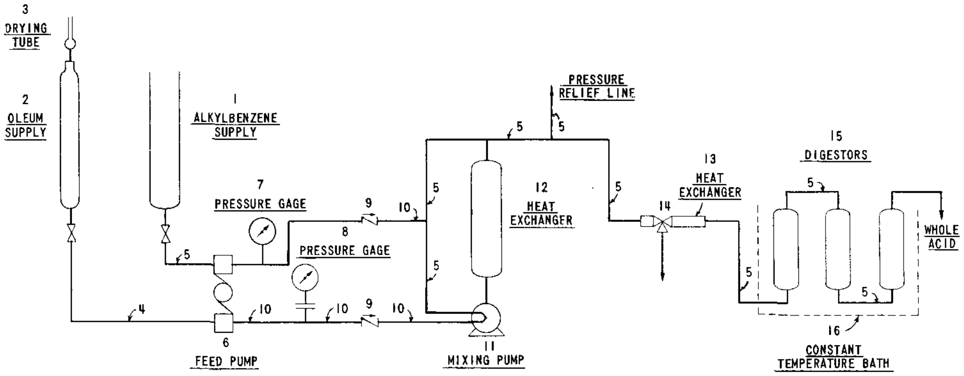

FIG. 2. Continuous oleum sulfonation unit.

Equipment (See corresponding number in schematic)

1. 500-ml glass buret.
2. 250-ml glass buret with ⊤ female joint at top.
3. Drying tube with anhydrous calcium chloride.
4. Teflon tubing, 4.8 mm ID.
5. Polyethylene tubing, 4.8 mm ID.
6. Milton-Roy "Minipump," Model No. MM 2-B-99, ⅛-inch plunger on oleum side, ¼-inch plunger on alkylbenzene side.
7. Gage, 60-psi range.
8. Gage, 100-psi range, with 316 stainless steel protective diaphragm.
9. ⅛-inch, 316 stainless steel ball check valve. Ball loaded with 316 stainless steel spring to give about 30-psi back pressure.
10. 3.2 mm 316 stainless steel tubing. Oleum line extends to within about 1.5 mm of mixing pump impeller.
11. Eastern centrifugal pump, Model E-7, 316 stainless steel, with mechanical rotary seal and Teflon packing. Pump speed is regulated with a variable transformer.
12. Water-cooled glass heat exchanger (length 20 cm, outside diameter 3.3 cm) with internal cooling coil wound from 140 cm of tubing; annular space coil to wall, 2 mm; thermowells at top and bottom; product vol, 70 ml; total product vol including pump and recycle line, 115 ml.
13. 15-cm long, 9.5-mm OD glass tubing wrapped with a heating tape (10 ohms). Heat input is regulated with a variable transformer.
14. Three-way stopcock.
15. Glass digestor tubes, 15-cm length by 3.8-cm diameter, with thermowells. Total vol of digestors and connecting tubing is 560 ml.
16. Const temp bath.

and between any of the digestors. If a high active slurry is necessary, the sulfonic acid can be diluted batchwise with water, settled to give a spent acid strength of 79%, and then neutralized as in the batch oleum method.

Discussion of Procedure. The continuous oleum sulfonation method was developed because sulfonates from commercial detergent operations using different commercial alkylbenzenes were reported to have a larger variation in unsulfonated oil contents than found in the batch sulfonation. Our laboratory results confirm that the continuous unit is more sensitive in showing the differences among alkylbenzenes with respect to oil content.

In Figure 3 and Figure 4, the effect of digestion time on unsulfonated oil content is shown at oleum/alkylbenzene mole ratios of 3.2 and 3.0. In these figures, the 5–6 min holdup time in the mixing loop (sulfonator) is not included. The difference in behavior between the five samples is quite striking. For instance, at an oleum/alkylbenzene mole ratio of 3.2 (Figure 3), an oil content of 0.6% was obtained after only 9 min digestion with Alkylbenzene A as compared to 1.6–3.1% unsulfonated oil for the other samples. The significant effect of oleum/alkylbenzene ratio is also apparent from a comparison of Figure 3 and Figure 4. We did not investigate the reason for the differences in unsulfonated oil contents of the various samples. Mol wt would be expected to be a variable affecting the degree of sulfonation. However, in our study, Sample E with the highest mol wt sulfonated to a lower oil content than Samples B, C, and D, indicating that variables other than mol wt affect the unsulfonated oil contents of detergent alkylbenzenes.

Batch SO_3-Air Sulfonation

Experimental Procedure. The apparatus for laboratory batch SO_3-air sulfonation is shown in Figure 5, and the major items of equipment are described.

All glass joints in the equipment are liberally sealed with Halocarbon stopcock grease, and the syringe plunger is lightly lubricated with the same unreactive material. The stirrer shaft is lubricated with the alkylbenzene being sulfonated. Dried air is started through the apparatus at a rate of 20 ml/sec; alkylbenzene (0.39 mole) is charged through a funnel inserted into the vent in the reactor. The vaporizer heat is turned on, the alkylate is stirred at 800 rpm, and the reactor jacket is filled with 102F

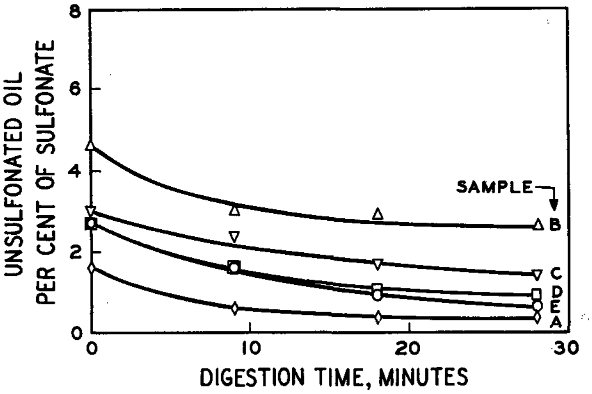

FIG. 3. Continuous oleum sulfonation; unsulfonated oil content vs. digestion time; sulfonating agent/alkylbenzene mole ratio of 3.2:1.0.

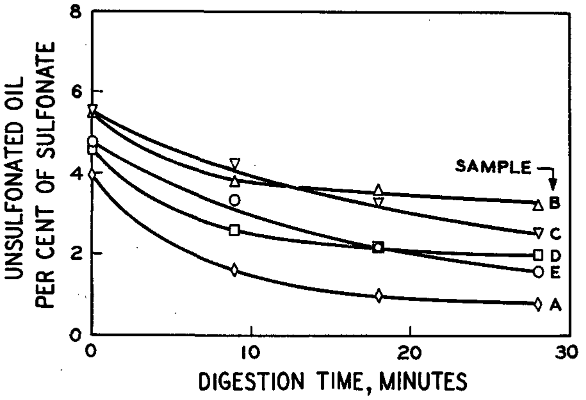

FIG. 4. Continuous oleum sulfonation; unsulfonated oil content vs. digestion time; sulfonating agent/alkylbenzene mole ratio of 3.0:1.0.

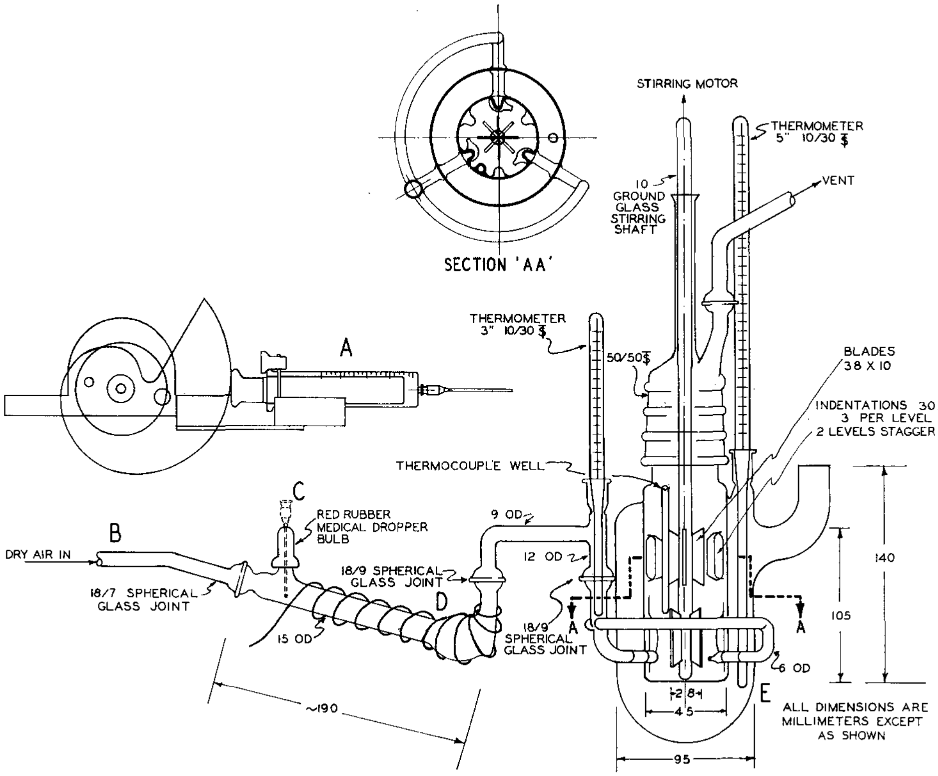

FIG. 5. Batch SO_3-air sulfonation equipment.

Equipment (See corresponding letter in schematic)

A. Microchemical Specialties Co. Syringe Feed Device. It is equipped with a No. 13 cam and a 20-ml syringe which delivers 19 ml of liquid SO_3 in approx 57 min. The needle is a 2-inch No. 18 gage, cut square on the end.

B. Air inlet tube. The air is dried by passing through concentrated sulfuric acid and anhydrous calcium chloride, and is controlled by a reduction valve, and measured by a calibrated orifice manometer filled with detergent-range alkylbenzene.

C. Rubber diaphragm made from a red rubber medical dropper bulb with the open flange cut off.

D. SO_3 vaporizer made from Pyrex glass and wound with electrical heating tape (12 ohms). The heat to the vaporizer is regulated with a variable transformer so that the air-SO_3 stream entering the reactor is 160–170F. (The temp of the vaporizer is not critical as long as the liquid SO_3 is immediately vaporized upon injection and the temp of the air-SO_3 stream is within the limits noted above.)

E. Jacketed SO_3-air sulfonation reactor made from Pyrex glass. Critical dimensions are shown in schematic.

water. The syringe is filled with 19 ml (36 g, 0.45 mole) of stabilized liquid SO_3, the needle is inserted through the rubber diaphragm so that the point touches the opposite side of the vaporizer, and the syringe is clamped tightly in position on the feed device.

The air rate is increased to 160 ml/sec, and the feed device is started. After all of the liquid SO_3 is injected ($\sim$ 57 min), the vaporizer heat is discontinued, the stirrer stopped, and the air disconnected. The sulfonic acid is poured into a 250-ml beaker and stirred while 15 ml of distilled water is added over a period of about 10 min (maximum temp of 130F). This treatment decomposes the sulfonic acid anhydrides formed during the sulfonation (1). Neutralization of the sulfonic acid is accomplished as for the batch oleum sulfonation method, except 150 ml of 6.7% aqueous NaOH is used. The resulting sulfonate slurry contains about 35% sodium alkylbenzenesulfonate and has a sulfonate/sulfate ratio of about 97:3.

Discussion of Procedure. Both the SO_3:air ratio and the SO_3:alkylbenzene ratio must be closely controlled in the batch SO_3-air sulfonation procedure. Because high SO_3:air ratios are detrimental to sulfonate color (1,3,4,5), the SO_3 is vaporized in a stream of clean dry air to a maximum concentration of six wt per cent. This percentage of SO_3 in air is maintained by injecting liquid SO_3 into the heated vaporizer at a const rate while the rate of air flow is also controlled at a const level. The SO_3 is vaporized immediately on injection into the vaporizer, and thus the possibility of buildup or fluctuations in the SO_3 concentration is minimized.

The sulfonating agent:alkylbenzene ratio is more critical in SO_3 sulfonation than in either batch or continuous oleum sulfonation. The ratio used in this method (1.14:1.00) was determined experimentally by varying the SO_3:alkylbenzene proportions for a high quality dodecylbenzene of 246 average mol wt (Alkylbenzene A in Table III) and selecting the ratio giving the best combination of low unsulfonated oil content and low solution color (Figure 6). Lower SO_3:alkylbenzene ratios give lower colors but higher oils, while higher ratios of SO_3 give darker colors and also higher sodium sulfate contents (Table I). This latter effect is particularly detrimental if the SO_3-air sulfonate is to be used in liquid detergents.

The optimum ratio of SO_3:alkylbenzene used in this method is somewhat higher than that reported previously by Gilbert (4); however, this is probably due to a greater loss of SO_3 in the air stream in this procedure.

Temp of the sulfonation reaction in the method is not controlled except by the moderating influence of the 102F water in the jacket surrounding the reactor. However, the temp of the mixture normally rises from 102F to about 122F during the course of the SO_3 addition. This temp range is optimum for SO_3-air sulfonation; lower temp tend to give more sulfonic acid anhydride formation, while higher temp result in sulfonates of poorer color (4,5).

This laboratory method is used routinely to evaluate alkylbenzenes with average mol wt from 235–270 by using the same mole ratio of SO_3:alkylbenzene (1.14:1.00). However, for very high average mol wt alkylbenzenes, such as pentadecylbenzenes, the

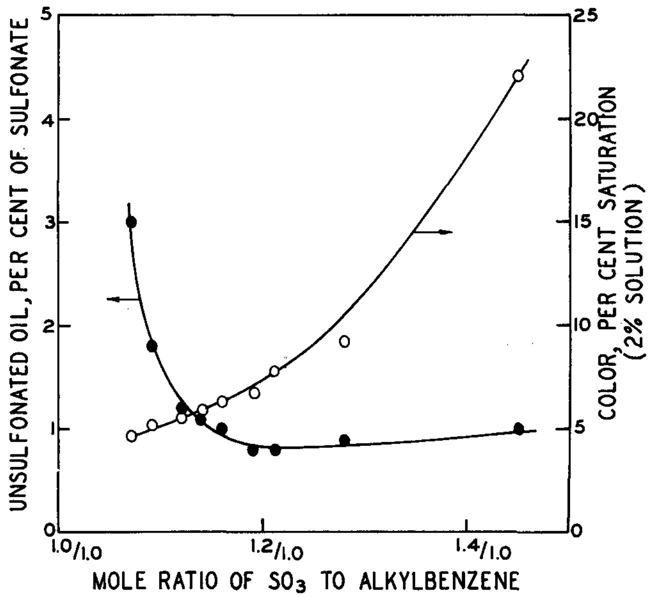

Fig. 6. Effect of SO_3: alkylbenzene ratio on sulfonate oil and color.

mole ratio of SO_3:hydrocarbon must be increased in order to get realistic unsulfonated oil contents (Table II). Necessity for this adjustment is possibly due to the sulfonic acid viscosity of the very high mol wt alkylbenzenes. These high viscosities result in poorer mixing, poorer contact between SO_3 and alkylbenzene, and thus less efficient utilization of SO_3.

Analytical Methods

Sulfonate Quality Evaluation. The quality of the sulfonates prepared by these laboratory methods is evaluated by determination of the unsulfonated oil contents and solution colors. Unsulfonated oil content is determined by extraction with petroleum ether or isopentane from 70% ethanol solution, followed by weighing the residue after evaporation of the solvent on a steam bath (7). The colors are measured in terms of the internationally defined ICI tristimulus system (6). In practice, the colors of 2.0% sulfonate solutions are expressed in terms of per cent saturation (or per cent purity) (7). The higher the per cent saturation, the poorer the color.

Low inorganic sulfate content is another important quality factor for liquid detergents. Sodium sulfonate:sodium sulfate ratios are determined by analyzing the sulfonation reaction mixture for sulfonic acid and for sulfuric acid. The sulfonic acid is determined by titration with standard quaternary solution (7) and the total acid by titration with standard sodium hydroxide solution. The difference between total acid and sulfonic acid is the sulfuric acid content. The inorganic sulfate content is calculated from the sulfuric acid percentage and is reported in terms of the sodium sulfonate:sodium sulfate ratio.

TABLE I

Effect of SO_3: Alkylbenzene Ratio on Sulfonate: Sulfate Ratio of Product

SO_3 : alkylbenzene mole ratio	Sodium sulfonate : sodium sulfate ratio	
	Alkylbenzene A (avg MW = 246)	Alkylbenzene E (avg MW = 267)
1.14	97 : 3	97 : 3
1.28	96 : 4	97 : 3
1.45	93 : 7	93 : 7

Alkylbenzene Bromine Numbers. Bromine numbers are determined by a modification of ASTM D 1159-59T (2). Modifications are:

1. The use of a 50:50 wt ratio of carbon tetrachloride/glacial acetic acid as the solvent.
2. Reaction of bromide-bromate with hydrocarbon at ice bath temp.

Comparison of Detergent Alkylbenzenes

Table III summarizes unsulfonated oil and color data for the five commercial Alkylbenzenes A, B, C, D, and E previously mentioned and for Alkylbenzenes F and G also commercially available. Variations in unsulfonated oil contents were fairly small employing batch oleum (1.0–1.8% of sulfonate) or SO_3-air (1.0–1.8% of sulfonate) sulfonation; but with the continuous oleum sulfonation method, more significant differences were obtained (0.4–2.6% of sulfonate).

For six of these alkylbenzenes, continuous oleum sulfonates were lower in color than the corresponding batch oleum and SO_3-air sulfonates. Colors of SO_3-air sulfonates varied more widely than colors of the oleum sulfonates, probably due to the sensitivity of the SO_3-air sulfonation method to alkylbenzene impurities. For example, SO_3-air sulfonation is very sensitive to unsaturates, as shown by the poor color of sulfonate from Alkylbenzene F (with a high bromine number of 0.13 cg/g). On the other hand, there is no apparent relationship between color and bromine number for the oleum sulfonation procedures. For example, Alkylbenzene F gives excellent sulfonate colors by both oleum sulfonation procedures.

TABLE II

Effect of Alkylbenzene Average Mol Wt on SO_3: Alkylbenzene Ratio Necessary for Laboratory Sulfonation of High Quality Alkylbenzenes

Alkylbenzene avg mol wt	SO_3 : alkylbenzene mole ratio	Unsulfonated oil content, % of sulfonate
246[a]	1.14 : 1.00	1.1
267[b]	1.14 : 1.00	1.3
279[c]	1.22 : 1.00	1.3
289[c]	1.22 : 1.00	1.4

[a] Alkylbenzene A, Table III.
[b] Alkylbenzene E, Table III.
[c] Experimental research alkylbenzene.

Comparisons of sulfonates made from the other alkylbenzenes also show interesting variations in qual-

TABLE III

Sulfonate Quality from Batch and Continuous Oleum Sulfonation and Batch SO_3–Air Sulfonation

Alkylbenzene			Oleum sulfonation[a]				SO_3-air sulfonation[b]	
			Batch		Continuous			
Identification	Bromine number, cg/g	Avg mol wt	Unsulfonated oil, wt % of sulfonate	Color, % saturation (2.0% solution)	Unsulfonated oil, wt % of sulfonate	Color, % saturation (2.0% solution)	Unsulfonated oil, wt % of sulfonate	Color, % saturation (2.0% solution)
A	0.02	246	1.0	6	0.4	3	1.1	6
B	0.01	258	1.3	7	2.6	4	1.5	8
C	0.02	258	1.5	9	1.4	6	1.8	8
D	0.03	258	1.1	10	0.9	6	1.7	15
E	0.02	267	1.0	6	0.7	4	1.3	7
F	0.13	241	1.0	4	0.4	5	1.0	25
G	0.05	261	1.8	9	1.6	8	1.3	13

[a] Oleum/alkylbenzene mole ratio: 3.2 : 1.0.
[b] SO_3/alkylbenzene mole ratio: 1.14 : 1.0.

ity. Alkylbenzene B gives fairly good colors by all three sulfonation techniques but high oil contents, while Alkylbenzene D gives low oils when oleum sulfonated but high oil content and a poor color when SO_3-air sulfonated. Alkylbenzene G gives fair colors but high oils by the oleum methods and a poor color on SO_3-air sulfonation. On the other hand, Alkylbenzenes A and E gave good colors and low oils by all three sulfonation procedures.

It is evident that sulfonate quality obtainable from any particular alkylbenzene is greatly influenced by method of sulfonation. Variation in alkylbenzene most strongly affects the colors of SO_3-air sulfonates and the oil contents of continuous oleum sulfonates. However, the two effects are apparently not related, as the same alkylbenzenes are not necessarily poor in both qualities. Except for the above-mentioned relation, no effective general correlations between alkylbenzene inspections and sulfonate quality appear to exist. Thus, it is not yet possible to accurately predict alkylbenzene sulfonation performance without actual sulfonation tests. Small-scale sulfonation methods as described in this paper are therefore most useful in predicting sulfonate quality.

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Bleaching of Refined Cottonseed Oil with Modified Alumina Adsorbents[1]

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Abstract

Activated aluminas, modified by treatment with inorganic and organic acids were tested for their efficiency as bleaching agents and for their ability to eliminate the response of refined cottonseed oil to the Halphen test. The best of these adsorbents, an alumina containing catalytic amounts of adsorbed sulfurous acid, is a bleaching agent that is effective in removing problem pigments from off-colored cottonseed oils, and is superior to activated aluminas in removing green chlorophyll-like pigments. Oils bleached with the catalytic adsorbent are negative to the Halphen test, and are free of sulfur.

Study of the rate of reduction in the Halphen test response as a function of bleaching time and temp indicated that sulfurous acid treated alumina has a pronounced catalytic effect. The Halphen test response is eliminated during a 30 min bleaching period at 225C. Deodorization conditions employed had little effect on Halphen test reduction.

Introduction

ADSORPTION BLEACHING of refined cottonseed oil is practiced for the purpose of removing objectionable red, yellow, and green color bodies from the oil. However, the Bentonites and Fullers earths normally used for this purpose have little, if any, affinity for the refractory red color bodies which occur in about 25% of the domestically produced oils (7). Such oils are termed "off-color" refined oils.

Finely ground activated alumina was found recently to be superior to both Natural and acid activated Fullers earths for removing the red "problem" pigments from off-color refined cottonseed oils (7). Alumina, however, must be employed in conjunction with small amounts of activated carbon to remove the green chlorophyll-like pigments which occur in some refined oils (7).

Cottonseed oil, and the seed oils of seeds from many plants of the order *Malvales*, give a positive Halphen test. These oils turn red when they are heated in the presence of sulfur and carbon disulfide (1,4). It is generally assumed that this test is specific for fatty acids containing a cyclopropene ring.

Although the removal of the Halphen test response is not generally an objective of the bleaching process, adsorbents which are efficient both for the removal of objectionable pigments, and the Halphen test response, would materially broaden the scope of the bleaching process.

In the studies reported here, on the evaluation of acid modified aluminas, a catalytic sulfurous acid-treated alumina adsorbent was found to be efficient for removing green chlorophyll-like pigments as well as objectionable red and yellow pigments from refined cottonseed oil. Oils bleached with this adsorbent were found to be negative to the Halphen test, and free of sulfur.

Materials and Methods

The several modified alumina adsorbents used in the present study were prepared from a commercial activated alumina which was ground in a ball mill to pass a 400 mesh screen. The particle size distribution of this stock alumina, and of official AOCS Natural Earth (1) are reported in Table I. Fifty-g por-

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[1] Presented at the AOCS Meeting in New Orleans, 1962.

[2] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U.S.D.A.