The Journal of the American Oil Chemists' Society

Volume 33 FEBRUARY, 1956 No. 2

A Continuous Process for Synthetic Detergent Slurries[1]

HAROLD E. HUBER JR., PETER J. BAKER,[2] and P. B. SCHMIDT JR., The Girdler Company, Votator Division, Louisville, Kentucky

THE RECENT GROWTH of the synthetic detergent field, both in this country and abroad, has intensified the interest in the development of a new and improved method of carrying out and controlling sulfonation and sulfation reactions. As a result of this, a program was initiated to study in detail the effect of operating variables of a scraped surface continuous reactor on the sulfonation of alkyl aromatics. Results were so promising that the investigation was expanded to include the other unit operations necessary to prepare a high active synthetic detergent slurry. Many months of concentrated pilot plant and engineering study were involved in this investigation; and the work, aided by previous experience gained in the design and construction of continuous reactors, resulted in a finished continuous process capable of producing a slurry of excellent properties.

The heart of the process is a multiport injection reactor which is employed in the major steps. The function of this unit will be explained in detail under sulfonation. Although the operation which we shall describe is a continuous, straightforward process, we shall divide it into five distinct steps, each of which can have an effect on the finished product.

In general, our main objective is to realize a final slurry that has good color, low free oil, and a complete absence of odor. In addition to this, our secondary objective is a continuous process that is independent of the human element and that results in a uniform product of the desired active level which is white and does not require bleaching. The particular process on which we devoted our time is based on the sulfonation of dodecylbenzene with 20% oleum followed by digestion, dilution, separation, and subsequent neutralization with 18 to 20% sodium hydroxide. Other materials have been used for the various reactants; however space does not allow us to do any more than mention these.

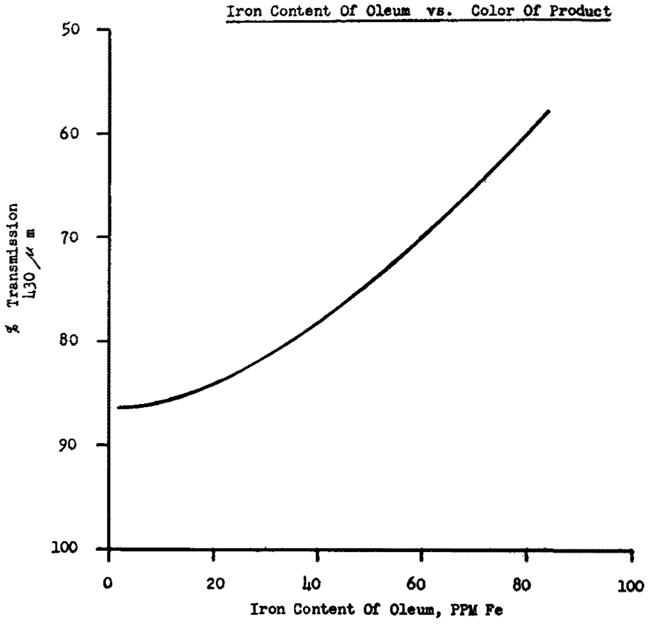

FIG. 1. Color vs. iron content of oleum.

The production of high active slurry, using oleum, requires five distinct steps, all of which will be discussed in detail. Table I gives the rates of the various streams and the product analysis for the small size commercial plant designed for the production of 500

TABLE I

Product Streams

Continuous Sulfonation Process; Sulfonation of Alkyl Benzene with 20% Oleum Composition of Product Streams

	Feed To Sulfonating Unit	Discharge From Digester Tank	Feed To Dilution Unit	Discharge From Dilution Unit	Overflow From Settling Tank	Spent Acid Discharge	Feed To Neutralizing Unit	Product	Product: % Composition As Discharged	Product: % Composition Dry Basis
Alkylate Lb. (M.W.: 232)	350	3.5	3.5	3.5	3.5	......	3.5	3.5	0.3	0.6
Oleum Lb. 104.5% H_2SO_4	437.5	......	......	......	......	......	......	......	......	......
Sulfuric Acid Lb. Y % H_2SO_4	......	317.6 (97.9%)	317.6 (97.9%)	399.0 (78%)	64.43 (78%)	334.57 (78%)	64.43 (78%)	......	......	......
Sulfonic Acid Lb. RSO_3H	......	466.4	466.4	466.4	464.07	2.33	464.07	......	......	......
Sodium Sulfonate No. RSO_3Na	......	......	......	......	......	......	......	496.0	45.5	86.7
Caustic Sol. Lb. X % NaOH	......	......	......	......	......	......	558.0 (18%)	......	......	......
Sodium Sulfate Lb.	......	......	......	......	......	......	......	72.8	6.6	12.7
Water	......	......	81.4	......	......	......	......	517.7	47.6	......
Total Lbs./Hr.	787.5	787.5	868.9	868.9	532.0	336.9	1090.0	1090.0		
Approximate Density		1.242			1.02	1.73		0.75 to 0.9		
Approximate Visc.		600 cp 80°F.			400 cp 130°F.			2500 to 8000 cp		

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[1] Presented at the 46th annual meeting, American Oil Chemists' Society, New Orleans, La., April 18-20, 1955.

[2] Present address: Mobay Chemical Company, Anniston, Ala.

lbs. per hour of active material. One point that should be brought out is that, when sulfonating with 98% acid, the entire plant can use city water in place of refrigeration, which in some instances would result in a considerable saving in processing costs. Should a low active product be desired, then the dilution and separation steps can be omitted. In general, we shall discuss the high active product as it is the one of more general interest and the one that is harder to make.

Introduction

The first, and also generally considered the most critical, step is sulfonation. It is here that the overall yields and the odors are basically controlled, and it is also here that the color quality can be lost by secondary reactions. In order to realize the best product it is, of course, necessary to have raw materials of high standards. This applies not only to the alkyl aromatics but also to the oleum. The dodecylbenzene no longer appears to be a problem; however the oleum can cause some trouble if extreme care is not taken, especially where relatively small quantities of oleum are used. In these instances the acid used should have a minimum amount of storage in iron drums; and a close check should be made on all iron contents. Figure 1 shows the change in light transmission or color of the finished product due to change in iron content of the oleum feed. Standard specifications should call for iron below 40 parts per million. If the acid is received direct from the manufacturer in stainless steel cars or trucks, then low iron content is not a problem.

Step A—Sulfonation

A dodecylbenzene cut and the 20% oleum are brought together in the desired proportions in a specially designed continuous reactor, which is equipped with a multiplicity of injection ports. An artist's conception of one form of this reactor is shown in Figure 2. In this particular instance the alkyl aromatic is passed through the product annulus; and the acid is injected through the ports or orifices, which can be located in either the shaft or the jacket, depending upon the particular unit employed. As the reaction of the alkyl aromatics and the oleum occurs rather rapidly under the conditions employed, the tendency of overheating and side reactions is limited by controlling the amount of acid at any one point. This is done by injecting about one-quarter of the total acid into the first part of the turbulent zone, thus, in effect, providing a large excess of the alkyl aromatic as a diluent. At the same time the violent agitation afforded by the revolving shaft gives maximum dispersion between the acid and the alkalate phase. In addition to this, the scraped surface principle results in rapid removal of the exothermic heat of reaction, thus affording excellent temperature control. At a point approximately one-fourth the length of the reaction zone an additional one-quarter of the acid is injected. At the halfway point in the reactor the remainder of the acid can be injected. The dilution afforded by both the spent acid and the sulfonic acids previously produced prevents local overheating and loss in color. At the exit of the multiport injection reactor the reaction is from 85 to 95% complete, depending upon the temperature level at which the sulfonation is controlled and upon the acid to alkylate ratios used.

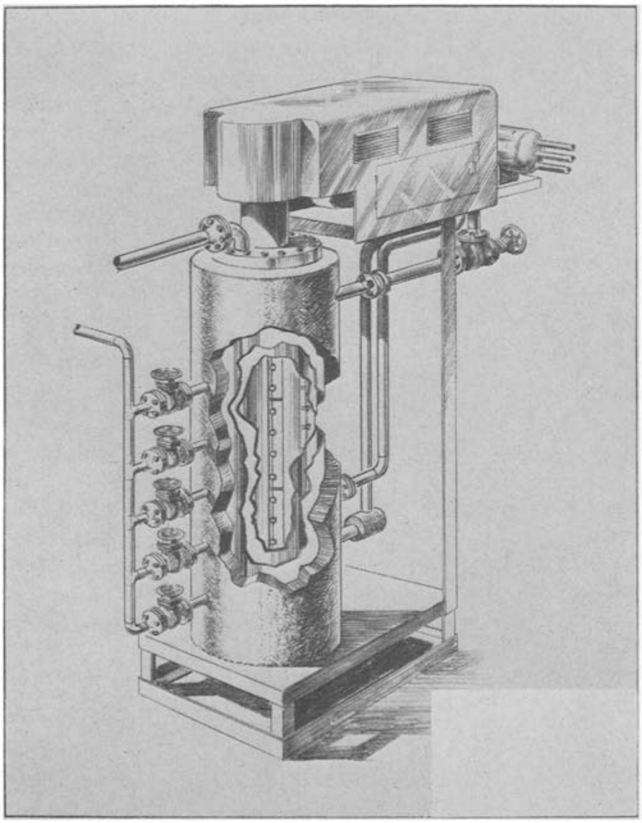

FIG. 2. Multiport injection reactor.

The conversion *versus* the sulfonation temperature is shown in Figure 3. As it is always desirable to obtain the maximum yields on feed, the ideal situation would be to increase the temperature of sulfonation to that point where yields begin to fall off, thus indicating secondary reactions such as the dealkylation of the alkyl aromatic.

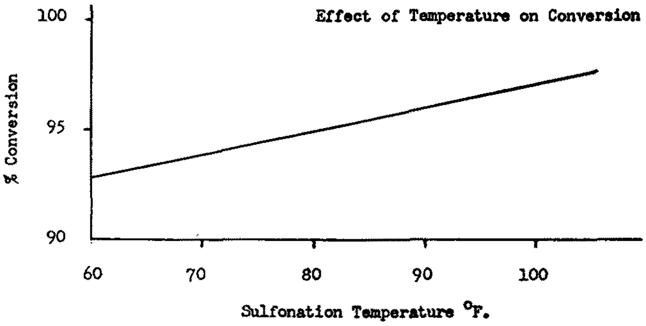

FIG. 3. Sulfonation temperature vs. conversion.

Figure 4 shows the effect of sulfonation temperature on free oil at two different acid ratios. The aging time in this instance was only 6 min. Should these same data be taken after a 40-minute digestion period, the curves would be considerably lower; however their general shape and the temperature of minimum free oil would be approximately the same. Using these curves alone, a temperature between 90 and 100°F. would be chosen for the optimum conditions for sulfonation; however we find that in general when using 20% oleum and when digesting for a sufficient period to give a final free oil content of approximately .6% on a dry basis, it is necessary to

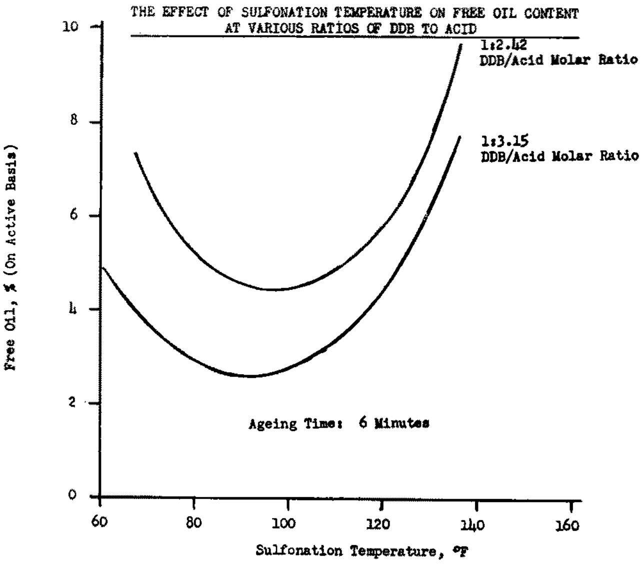

FIG. 4. Sulfonation temperature vs. free oil.

sulfonate somewhere around 80°F. in order to prevent loss in color. Thus, from the above, we find that the optimum operating conditions are not dependent upon a single variable, but upon acid ratios, sulfonation temperatures, and digestion periods.

Step B—Digestion

As mentioned previously, under the conditions chosen the reaction is approximately 90% completed. To carry the conversion to 98 to 99% requires a digestion period of approximately 40 min. The effect of digestion time *versus* free oil, which is the indication of conversion, is shown on Figure 5. This series of three curves indicates the effect of temperature on free oil as the digestion period, or aging time, is varied. This first series of curves was obtained with a single-point injection wherein the total quantity of acid was injected along with the dodecylbenzene at the inlet of the sulfonation reactor. The break in the 92°F. curve under these conditions of operation is apparently due to dealkylation. The lower curve shown in this figure indicates the effect of going from a single-point injection to a multipoint injection. From this it can be seen that free oil *versus* aging times does not change appreciably after approximately 1 hr. Experiments have indicated that with this improved method of injection acceptable products can be obtained at higher sulfonation temperatures. Referring again to Figure 4, it is also noted that the original acid-to-alkylate ratio will decrease the digestion period. Color deteriorates with increased length of holding time as well as with the increase of alkylate-to-acid ratio and the increase in sulfonation temperature; thus we find that the color factor again is responsible for the correct balance between temperature and the digestion period.

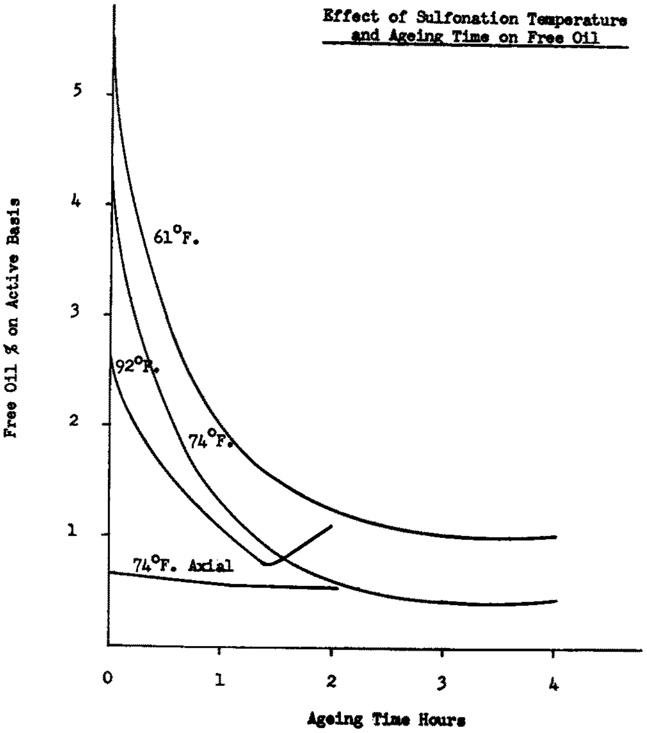

FIG. 5. Time vs. free oil.

The extreme mixing afforded during the sulfonation step results in a sulfonic acid-sulfuric acid mixture that will not separate during the digestion period. This is true even for the single-point injection. For that reason, this part of the process equipment consists merely of an expanded section or tank, and at this point neither agitation nor heating is required. The temperature rise due to the reaction's going to completion is anywhere from 10 to 15°F., when using 20% oleum to sulfonate.

Step C—Dilution

Dilution is required in high active production, for without it a separation cannot be obtained between the sulfonic acids and the large excess of sulfuric acid that it is necessary to add in the sulfonation step. When dilution is used prior to neutralization, it is found possible to separate the resulting mixture into two layers, the bottom layer of which is predominantly spent sulfuric acid, having a concentration of 78 to 80% while the top layer is a concentrated sulfonic acid mixture with from 11 to 12% sulfuric acid.

The highly exothermic nature of the dilution reaction can, if not properly controlled, result in color degradation of the product. The work during the development of this process has shown the necessity of using the multiport injection system. Here, also, is the most critical operation from a corrosion point of view.

A continuous stream equivalent to the combined streams of the sulfonation step is taken from the digester and metered with the appropriate amount of water into a multiport injection reactor identical in general overall design to that used in the first step. Here however it is desirable to construct the unit of alloy 20, whereas the reactor used in the sulfonation step is preferably constructed of 316 stainless steel. Here again, the intimate contacting of the material is made possible by the very violent agitation and the injection at a multiplicity of points. In this instance the water is metered through the ports while the material from the digester is brought through the main inlet to the annulus. In general, the dilution is carried out in such a manner that the outlet temperature is in the range of 130 to 135°F., and the resulting spent acid from the separation step is approximately

78% after 4 hrs. The choice for the above conditions will be explained in the separation step.

The foregoing procedure is used for the production of high active slurries. When low active materials are desired, the mixed acids are pumped directly to the neutralization step from the digester.

Step D—Separation

The effluent from the dilution reactor is passed directly into a tank with a capacity equivalent to approximately four to six times the hourly volumetric flow from the dilution step. The design of this tank should be such that it has a relatively large area of interface to the total volume. With such design the surface of the sulfonic acid layer is at a minimum distance from the interface separating the acid layers. The tank itself is equipped with a means of external heating in order to maintain the temperature of the entire mass at the optimum conditions for rapid separation. As the rate of separation for a given dilution is a function of the mass temperature, it is desirable to go to as high a temperature level as possible; however, as the temperature is raised, the color of the final product will deteriorate. Another factor that is important at this point is that for any given temperature level the color of the final paste will be a function of the time. Thus it is necessary to find the optimum temperature that will give the best balance point due to loss in color by separating time and loss in color due to temperature. For the process that is outlined for 20% oleum this appears to be around 130 to 135°F. In this temperature range it requires about 4 hrs. for separation sufficient to gve a final paste of 86 to 88% on a dry basis. Higher active-ingredient materials are possible by adjusting the conditions during the dilution and separation; however it is felt that the loss in final color would not warrant increase in temperature or longer holding time, which would not result in a product greater than 92% active ingredient.

An alternate method of separation may employ a centrifuge immediately following the dilution step. In this instance sufficient water would be added to the dilution reactor to give a spent acid of approximately 82 to 83%. At dilutions above this percentage the loss of sulfonic acid to the acid layer becomes excessive while at figures below this the corrosive effect on the centrifuge increases.

The main problem is to find a centrifuge constructed of materials having the required tensile strength and at the same time having resistance to corrosion from the acid components. Another disadvantage in the centrifuge is that capacities are usually not great enough for the quantities involved. Manufacturers of centrifuges have recently had some success in finding acceptable materials of construction for the centrifuge bowl; however the tank method will offer economical advantages that will be hard to surpass. The main attraction of the centrifuge separation is that it would result in a process that would keep a minimum amount of material in process at any one time, with the only lag in the whole operation being in the initial start-up, where approximately 40 min. are required in the digester. It is possible even to reduce the digester time to a matter of 1 or 2 min. by using a 2-stage sulfonation step.

Step E—Neutralization

Neutralization is carried out in the same type of reactor as is employed for sulfonation and dilution. In this instance the mixed sulfonic acids are taken from the top layer of the separation tank and injected through the multiports into the caustic being proportioned into the product annulus. By means of a temperature recorder controller at the outlet of the reactor the desired temperature is maintained on the neutralized product. During the early development an outlet temperature in the range of 80 to 85°F. was maintained, which necessitated employing 35°F. brine or chilled water on the neutralizer jacket. Since then, however, it has been found that by employing the multiport injection system an outlet temperature of from 130 to 135°F. can be used without losing color. This change has permitted the use of 70°F. water instead of refrigerated brine, and it also gives a more fluid paste, which is easier to handle in the building and drying steps.

Since the neutralization operation is conducted in a completely enclosed system and since this type of apparatus can handle viscosities much higher than are economically feasible in other types of equipment, it is possible to neutralize with concentrated ammonium hydroxide or even liquid ammonia. In the pilot plant 18 to 20% sodium hydroxide was generally used; however runs have been made with 28% ammonium hydroxide, ethanol amine, and caustic solutions up to 40%. With 18% sodium hydroxide the analysis on an "as is" basis will show .3% free oil, 45½% sodium sulfonate, 6.6% sodium sulfate, and 47.6% water. On a dry basis this means that the finished paste will have .6% of free oil, 86.7% sodium sulfonate, and 12.7% sodium sulfate.

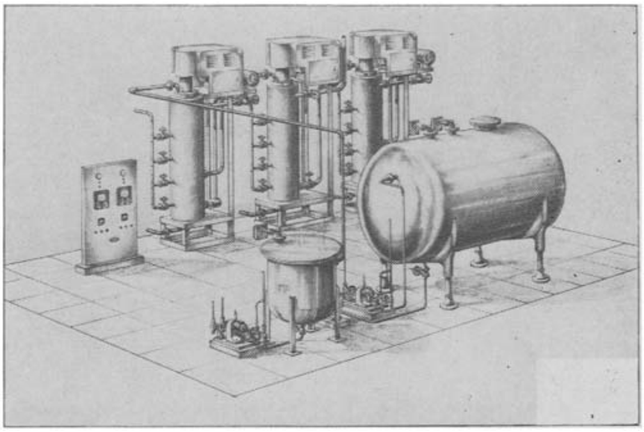

FIG. 6. 4,000-pounds-per-hour plant.

A complete plant for producing 4,000 lbs. per hour of active material is shown in Figure 6. This plant can be assembled in two standard bays of 18 ft. x 18 ft., giving a total floor space requirement of only 650 sq. ft. A smaller plant of 500 lbs. per hour active ingredient requires less than 200 sq. ft.

For low active slurries, that is for those operations in which the dilution and separation steps are not employed, the floor space requirements are reduced considerably.

[Received June 24, 1955]