Sulfation and Sulfonation

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THE principal industrial interest in sulfation and sulfonation in recent years has been in the production of synthetic detergents. Most of the products in this 1½ billion-pound-per-year field (4) are made by one or the other of these processes. Sulfated lauryl alcohol and sulfonated alkyl aromatics are typical products, both used extensively as the active ingredient in common household detergents. As processes, sulfation and sulfonation do not differ greatly. Both involve reaction of a raw material with strong sulfuric acid under similar operating conditions. Either process can be used to yield a wide variety of effective wetting agents, emulsifiers, or detergents, depending on the type of raw material. The distinction between the two is in the chemical structure of the product. In the sulfonation of an alkyl aromatic a carbon-sulfur linkage is obtained. In the sulfation of an alcohol, for example, a true half ester of sulfuric acid is formed with a carbon-oxygen-sulfur linkage. The difference in structure contributes to differences in properties, particularly in hydrolytic stability. Generally, however, the functional properties of the product are determined by the nature of the raw material being treated rather than by this structural difference. At the present time the most widely used materials are those produced by the sulfonation of alkyl aromatics.

Sulfonation

Aromatics. Prior to synthetic detergents the sulfonation of aromatics was practiced extensively in the dye industry. Through the sulfonic acid intermediary a wide variety of functional groups could be readily introduced into the aromatic ring. Sulfonation of benzene was also the basis of early phenol production and is still one of the major processes (11). Owing to this considerable industrial importance, sulfonation has been extensively studied; processes and variations of processes number in the hundreds. A comprehensive review of this work is now published yearly (7, 12, 13).

A basic process for the sulfonation of a simple aromatic, such as benzene, consists of adding 1½ to 2 moles of 98-100% sulfuric acid to a mole of benzene, refluxing the mixture, and finally heating to 150-200° F. to complete the reaction. Total batch time on a commercial scale may be 3 to 8 hours. During the reaction the water which is liberated dilutes the sulfuric acid and renders it less effective as a sulfonating agent. Below 75-80% acid strength the sulfonation of benzene proceeds very slowly, hence the need for excess acid. The major objections to this simple process are a) inefficient use of sulfuric acid, b) complications introduced by the presence of the excess acid in the product, and c) extended batch time. These same objections will be seen to carry over into detergent production. Several improvements have been made in this process. For sulfonating benzene or other easily vaporized aromatics, the use of the Tyrer process reduces acid requirements to 95% of the theoretical (8). With this system benzene vapor is introduced into 90% sulfuric acid maintained at about 200°F. Unreacted benzene vapor and water vapor are removed from the top of the vessel, condensed, and the benzene

phase recycled. For high boiling aromatics the charge may be blown with air or inert gas, or an additional volatile solvent such as low boiling hydrocarbon may be added to obtain the partial pressure effect.

Continuous benzene sulfonation is achieved in the Dennis-Bull process wherein concentrated sulfuric acid, or oleum, and benzene flow countercurrently (11). This method depends upon the fact that benzene sulfonic acid, not normally soluble in benzene, is dissolved to the extent of 2 to 3% in the presence of sulfuric acid. The 2 to 3% benzene sulfonic acid in benzene solution is taken off at the top of the reactor and separated by water washing while a 75-80% sulfuric solution is withdrawn at the bottom. In addition to these processes used for benzene sulfonation, others involving use of stronger sulfonating agents, sulfonation catalysts, and dehydrating agents have been proposed, some particularly for detergent production. These are discussed in the following section.

Alkyl Aromatics. Alkyl aromatics may be sulfonated over a considerable range of operating conditions, using acid strength from 98% sulfuric acid to free SO_3 and reaction temperatures from 20°F. to 140°F. However for detergent use there are quality considerations for the final product which restrict the combinations of these conditions that can be employed. In the manufacture of detergents it is usually preferable to sulfonate substantially to completion so that no additional processing is required to remove unreacted aromatics from the detergent product. At the same time there is continual desire on the part of the detergent producer to manufacture a product of light color and minimum odor, qualities usually achieved with mild sulfonation. As a result, sulfonating conditions in the range practical for detergents have been investigated quite fully in order to arrive at optimum combinations (16). A typical procedure for a commercial scale batch sulfonation in a plant as sketched in Figure 1 is as follows. The alkyl aromatic is charged to the sulfonator; an equal weight of 20% oleum is added slowly over a period of 1 to 1½ hours at a maximum batch temperature of 90°F. At the end of this time the reaction is about 90% complete. The acid mix is then allowed to digest for an additional 3 to 4 hours at 115°F. to complete the sulfonation to 97 or 98% reacted. This procedure yields a product which when neutralized contains about 2.0 to 2.3% residual oil on
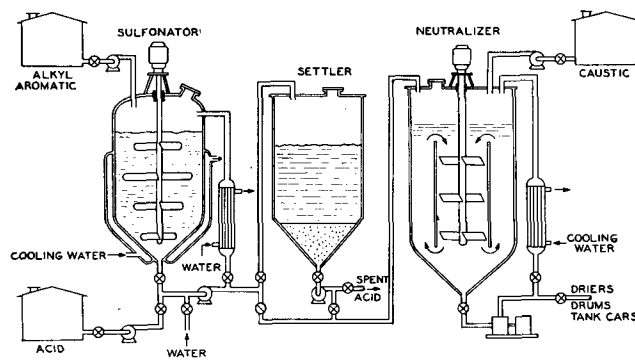

FIG. 1. Batch sulfonation plant.

the basis of the sulfonate and is satisfactory in color. By reducing the temperature during acid addition and digestion to 85°F. and increasing by about one-third the amount of acid used, the color can be improved and the oil content reduced to 1.4 to 1.7% on the basis of the sodium sulfonate. Further reduction in temperature to 50 or 60°F. with the same quantity of acid yields a sodium sulfonate practically white in color with a 1.6 to 1.9% oil content. These conditions are summarized in Table I. Figure 2 shows the effect

TABLE I

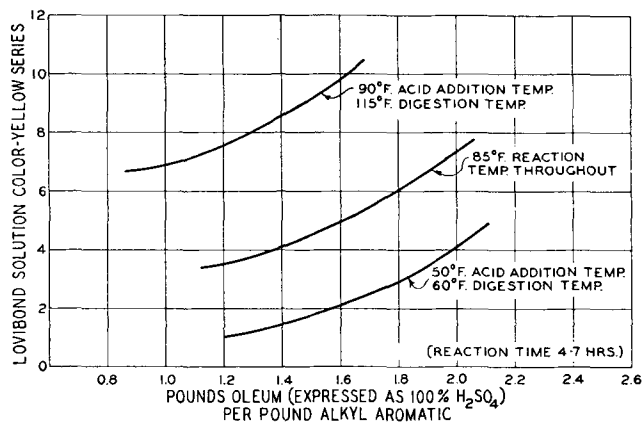|	Sulfonation, Temp., °F.		Reaction Time, Hrs.	Acid Strength % Oleum	Lbs. Oleum Per Lb. Aromatic	Color	Residual Oil, %
	Addition	Digestion					
1	90	115	4-6	22	0.98	Ivory	2.0-2.3
2	85	85	5	22	1.32	Pale Ivory	1.4-1.7
3	50	60	4	22	1.32	Ivory White	1.6-1.9

FIG. 2. Effect of ratio of acid to alkyl aromatic on color of sulfonate.

of the amount of acid and the reaction temperature on the color quality of the sodium sulfonate; Figure 3 illustrates the relationship between completeness of reaction, as measured by the residual oil content, and the color quality of the detergent. As the reaction is driven closer to completion (less residual oil), the color becomes progressively poorer. However at the lower reaction temperatures the rate of increase in color is not as great as at higher temperatures. The differences in product quality, although they may appear small, are significant to the detergent producer. The 85°F. system is quite frequently preferred for the production of household type detergents even though it entails use of more sulfuric acid. The 50-60°F. system has not been used commercially, principally because it requires a considerable revision in plant equipment which so far has not been considered justified.

During the early production of synthetic detergents the use of excess sulfuric acid was not a significant problem. The excess acid was neutralized with the sulfonic acid and the product marketed as a sodium sulfate-sodium sulfonate mixture. More recently, when it became desirable to add considerable amounts of phosphate builders to the detergent formulations, the presence of large amounts of sulfate interfered, and it then became necessary to consider means of reducing the sulfate content. The method now commonly used
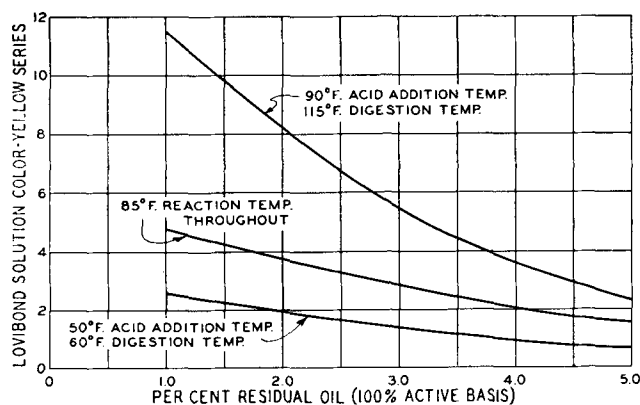

FIG. 3. Effect of per cent conversion of alkyl aromatic on color of sulfonate. (Constant reaction time-varying amounts of 22% oleum.)

consists of sulfonating with the excess acid, diluting the acid mix with water, and settling out a lower phase of sulfuric acid of about 80% concentration. The sulfonic acid is substantially insoluble in 80% sulfuric acid, and losses of sulfonic by this method are small. Settling is conducted at a temperature of 120° to 140° F. and requires 3 to 8 hours. Either batch or continuous phase separating may be used. After settling, the lower sulfuric acid phase is withdrawn, and the upper phase containing the sulfonic acid is neutralized to yield a product having a ratio of about 85 parts sodium sulfonate to 15 parts sodium sulfate on a dry basis. This sulfonate content is sufficiently high to permit easy use of the product in phosphate formulations. The spent sulfuric acid usually cannot be used again directly for detergent sulfonation but may be reprocessed or sold for less exacting uses.

In acid settling procedures it is preferable to limit the time and temperature as much as possible to minimize the formation of materials which contribute increased color to the neutralized product. The formation of color bodies is dependent on both these variables as shown in Figure 4.

The use of the elevated temperature (120-140°F.) in acid settling is necessary to reduce the viscosity of the upper phase and thus minimize the time required. Obtaining the reduction in viscosity by the addition of a solvent instead of by heating has been suggested and is effective. However the solvent must ultimately be removed from the product, and the additional process-
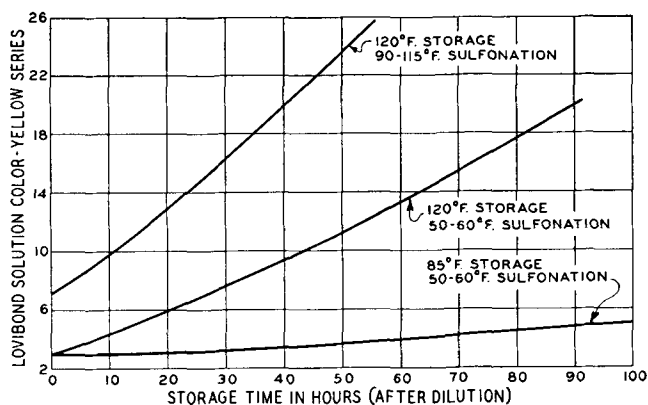

FIG. 4. Effect of storage of sulfonic acid on color of sulfonate.

ing involved on either the temperature sensitive sulfonic acid or the viscous neutralized slurry is a definite disadvantage. An extraction process has been proposed wherein concentrated hydrochloric acid is used as a wash to remove sulfuric acid; residual hydrochloric acid in the upper layer is removed by air blowing (5). Centrifuging of the acid appears to be a logical substitute for acid settling, but it is not yet practiced commercially. High corrosion rates in the centrifuge have been encountered in the brief test work done so far. The possibilities of eliminating acid settling by reducing the amount of excess acid used have been studied, following the approaches found practical in benzene sulfonation. The partial pressure systems used effectively in benzene sulfonations to reduce acid dilution usually cannot be applied directly to alkyl aromatic sulfonations. The alkyl aromatics tend to be high boiling materials of 500-600°F. boiling range. Performing the sulfonation at such a temperature that the aromatic contributes any substantial vapor pressure results in deterioration of the product. The aromatic itself is quite temperature-stable and is actually an overhead distillation product; however the sulfonic acid mixture is not correspondingly temperature-stable.

Employment of stronger sulfonating agents, stronger oleum and SO_3, to reduce residual inorganic acid is complicated by formation of undesirable disulfonates and sulfones. Direct use of oleums above 30% for sulfonation of alkyl aromatics for detergent use results in a product of poorer color. A further complication is the freezing point characteristics of oleum, solid above 60°F. between 30% and 58% SO_3 and above 75% SO_3.

Sulfur trioxide itself can be used for sulfonation, either in gaseous or liquid form, if used with a diluent to reduce oxidation, disulfonation, and other side reactions. The development of stabilized sulfur trioxide has increased the possibilities for commercial application of this method. A pilot unit for the study of vapor phase SO_3 sulfonation is shown on Figure 5 (6).
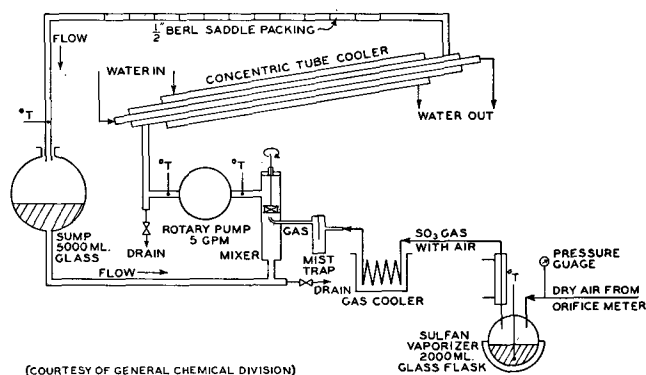
FIG. 5. SO₃ pump sulfonator.

Liquid SO_3 is vaporized by a stream of diluent air, cooled, and introduced into a small mixing chamber where it is contacted with the alkyl aromatic. The mix is then passed through a rotary pump, where the major part of the sulfonation occurs, and into a heat exchanger. From the exchanger the reaction mix is circulated to a sump and back to the inlet of the rotary pump. With this system agitation and cooling are

well controlled and only about a 10% excess of acid is required.

Alternative methods have been studied using liquid SO_3 with either light hydrocarbons or SO_2 as diluent. These systems are usually operated at low temperatures, the cooling being obtained by vaporization of part of the diluent. The diluent serves a triple function: provides cooling, reduces the severity of the sulfonation, and also reduces the viscosity of the reaction mix at the low temperature. A laboratory procedure used for an SO_3-SO_2 system consists of adding a 15% solution of SO_3 in SO_2 to the alkyl aromatic (16). The acid addition is extended over a 1-to-2-hour period, and the mix is then allowed to digest for an additional 2 to 3 hours. The temperature is maintained at 18°F. during the cycle by the evaporation of SO_2. Following digestion, the reaction is quenched with a small amount of water. The presence of water promotes the phase separation of the remaining SO_2 and also increases the mobility of the sulfonic acid layer. The product obtained by neutralization of the sulfonic acid is about 90% active (dry basis) and is of good quality, equivalent to that produced by the 50-60°F. sulfuric acid sulfonation. Figures 6 and 7 illustrate
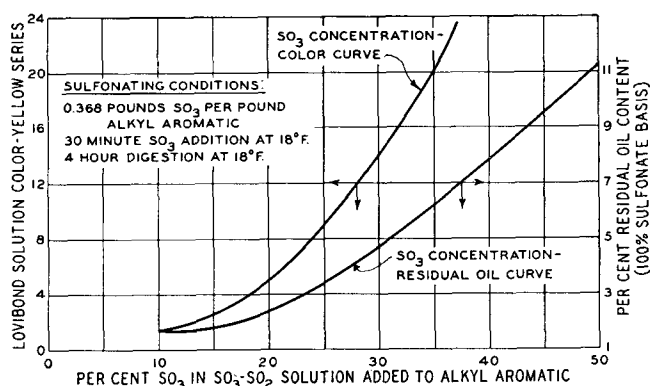
FIG. 6. Effect of concentration of SO₃ in SO₃-SO₂ sulfonating solution on color and oil content of sulfonate.

the important effects of the concentration of SO_3 in the SO_3-SO_2 solution and of the SO_3-hydrocarbon ratio on color and residual oil content of the neutralized product. If the concentration of SO_3 in the SO_3-SO_2 solution is increased materially over 15%, side reac-
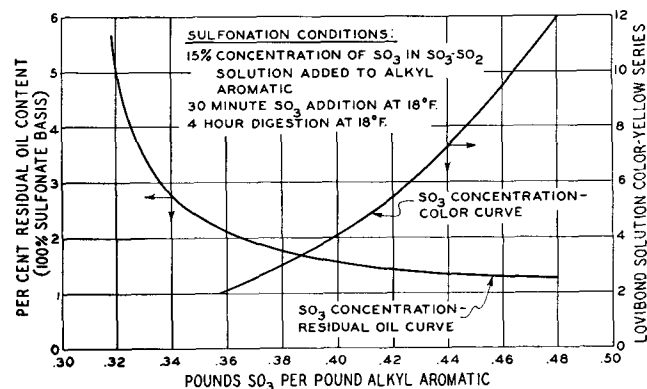
FIG. 7. Effect of SO₃ to alkyl aromatic ratio on color and oil content of sulfonate.

tions occur which produce color bodies and consume SO_3. The product is then high in color and residual oil. At present, most detergent sulfonations are performed with sulfuric acid or oleum; however the direct use of SO_3 in the now available stabilized form is one of the more interesting recent developments.

In addition to SO_3, numerous other sulfonating agents are being actively investigated for use in the detergent field, either with alkyl aromatics or with other hydrocarbons. Sulfuryl chloride, SO_2Cl_2, or mixtures of SO_2 and Cl_2 are being used commercially for the sulfonation of aliphatics (19). Sulfonyl chlorides were the basis of the German Mersol detergents and are of considerable industrial importance in this country. The reaction $RH + SO_2 + Cl_2 \longrightarrow RSO_2Cl + HCl$ is catalyzed by actinic light or by organic peroxides (9). The sulfonyl chloride product is hydrolyzed with caustic soda. Chlorosulfonic acid is also a strong sulfonating agent without the self-diluting effect of sulfuric acid. It reacts with hydrocarbons to form both mono and disulfonic acids and hydrocarbon-sulfonyl chloride. Like sulfur trioxide, chlorosulfonic acid is frequently used with an inert diluent. Acid sulfates and trihydrosulfates have specialized uses as sulfonating agents. They usually require temperatures of 200°F. or higher, which are normally impractical in detergent work. Acetic anhydride, phosphorous pentoxide, and boron trifluoride have been suggested as dehydrating agents for use in connection with sulfuric acid sulfonation to reduce the excess acid requirements. These and other sulfonation procedures are described in detail in the literature (7, 8, 20).

For commercial scale operations with sulfuric acid or oleum, glass-lined or stainless steel vessels are usually used. Stainless steel pumps, heat exchanger equipment, and lines are satisfactory.

Sulfation

In the production of surface active agents by sulfation, the raw materials most commonly used are naturally occurring oils and fats or base stocks synthesized from petroleum hydrocarbons. Generally the sulfation involves reaction of sulfuric acid with an hydroxy group or an olefin. In the naturally occurring oils and fats the functional groups used may either be present in the fatty acid side chain of the original glyceride or be introduced before sulfation by appropriate processing.

Examples of the types of raw materials used in preparing sulfates are given below.

1. Natural Oils and Fats. Sulfation occurs on the hydroxy or olefin group present on a fatty acid side chain to yield a sulfated glyceride. The preparation of Turkey Red Oil by the sulfation of the hydroxy group of ricinoleic glyceride in castor oil is typical.

2. Fatty Alcohols. These materials are prepared by the hydrolysis of glycerides to fatty acids and the reduction of the acid to alcohol by catalytic hydrogenation. Alternatively, the fatty alcohol may be made directly by the reduction of glyceride with metallic sodium (10). Sulfated products of this type, such as lauryl sulfate, are highly efficient detergents.

3. Monoglycerides. Fatty acids may be esterified with glycerol under controlled conditions to yield substantially the monoglyceride. One of the remaining hydroxy groups is then sulfated. Monoglycerides derived from coconut oil also yield effective detergents.

4. Fatty Olefins. Olefins used for sulfation may be naturally occurring, such as terpenes, or may be produced by decarboxylation of unsaturated fatty acids.

5. Alcohols and Olefins from Petroleum Stocks. Examples of these materials are alcohols derived from the Oxo process and olefins prepared either by polymerization of lower olefins or by cracking of wax (20).

In the sulfation of these raw materials the procedures used vary, depending on the quality requirements of the final product. For household type detergents it is important to obtain a product of good color and odor, whereas in the manufacture of a particular sulfated oil the major emphasis may be on controlling the degree of sulfation at some point short of completion to obtain desired performance characteristics. There is however a considerable amount of processing common to the preparation of these various sulfates and to the sulfonates previously discussed. The need for excess sulfuric acid, methods of separating excess acid after sulfation, and the removal of the heat of sulfation from materials usually temperature-sensitive are problems encountered to some extent in the manufacture of all of these products.

A simple sulfation cycle commonly used in sulfating oils consists of slowly adding 66° Bé sulfuric acid to the oil, maintaining a reaction temperature of 100° F. or less. The operation is usually batchwise, requiring 5 to 24 hours per batch. After sulfation, sodium sulfate or sodium chloride is added to salt out the sulfated oil. The oil is then further washed and neutralized with sodium hydroxide, carbonate, or ammonia.

This process is frequently modified by using stronger acid, i.e., 5 to 20% oleums, to improve the degree of sulfation and reduce time requirements. The amount of excess acid is again a variable controlling completeness of reaction. For materials especially temperature-sensitive, the reaction temperature may be reduced to 30°F. or lower (20).

For the production of sulfated monoglycerides a special process has been devised wherein the fatty triglyceride or fatty acid is reacted with glycerol and sulfuric acid all in one stage to yield the sulfated product. This is an economical process and is the basis of one of the popular household detergents. A continuous method, Figure 8, has been developed for this reaction in which the materials are introduced into the top of a tower and flow down over a series of cooling coils and paddles with continuous discharge from the bottom (14).
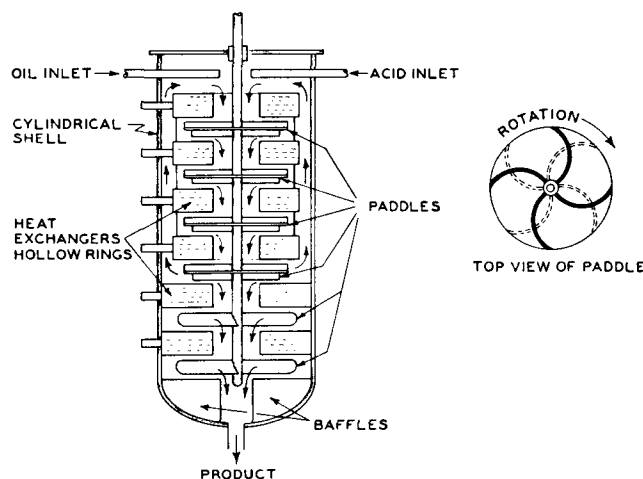

FIG. 8. Continuous sulfonator.

Most of the techniques used in connection with sulfonation have also been applied to sulfation. For instance, the use of sulfur trioxide with low boiling diluents to remove the heat of reaction and control the severity of sulfation has been studied (6). Sodium oleyl sulfate of 95% purity has been prepared by sulfation with pyridine-sulfur trioxide (1). An SO_3-dioxane complex is reported to be particularly effective in sulfating olefins (21). German industrial processes utilizing chlorosulfonic acid with coconut alcohols and pyridine-chlorosulfonic acid with oleyl alcohol have been described in the literature (2, 3).

Several novel reactor designs have been suggested to improve sulfation. A continuous process for the preparation of sulfonated or sulfated oils involves the use of a vertical tube reactor fitted with internal cooling coils. The tube is kept filled with acid; oil is pumped into the bottom of the tower, rises through the denser acid phase, and is withdrawn as partially sulfated oil (15). In another system, Figure 9, the sulfating agent and the fatty alcohol are introduced into a vessel in opposing spray patterns. The sulfate is formed and falls to the bottom of the vessel. Cooling is provided by a stream of air admitted at the bottom of the vessel and released at the top through a spray trap (17). The advantages of this procedure are the short reaction time and the intimate contact achieved with the acid, alcohol, and cooling medium. A varia-
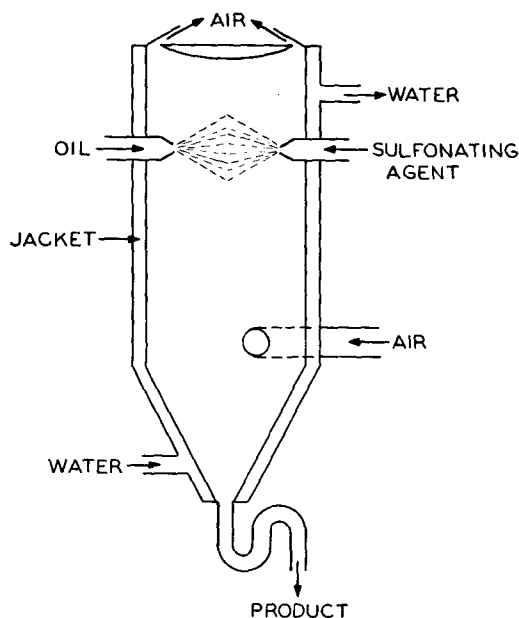

Fig. 9. Opposing spray continuous sulfonator.

tion of this method, Figure 10, consists of feeding the oil as a thin film on the jacketed wall of a vessel and spraying the acid onto the descending oil film. Cooling is achieved by circulating water through the jacket and also by an air stream circulated through the reactor (18).

The materials of construction of sulfation plants depend upon the particular oils to be handled. Monel equipment is generally satisfactory, but nickel clad equipment is preferred in handling some oils, such as olive oil. Glass-lined sulfators may also be used.
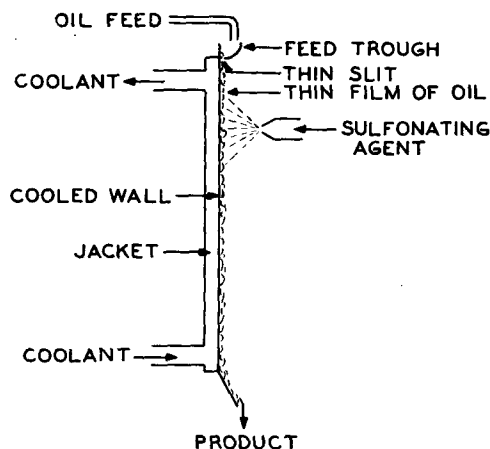

Fig. 10. Thin film continuous sulfonator.

Summary

Patent and technical literature contain a wide variety of references to sulfation and sulfonation. Many of these relate to methods specific for individual compounds or substituted functional groups, or to involved methods undesirable for commercial plant operation. Other references relate to gross methods wherein simplicity of operation is unrestricted by close product quality specifications. Sulfation and sulfonation for detergent manufacture fall in between these examples, being relatively straight-forward operations but subject to the strict requirements of good color and low residual oil content in the finished detergent. From the process standpoint, good color and low oil content tend to be opposing requirements. To achieve both requires careful selection and control of the process variables. There still remains much room for improvement in the techniques of detergent manufacture directed toward the economical use of time, equipment, and materials. Since this industry is relatively new and highly competitive, such developments may be expected.

Acknowledgment

REFERENCES

1. Anon., Oil Paint and Drug Reporter, 160, No. 16, 4 (1951).
2. Baird, W., U. S. Dept. of Comm. O.T.S. Report PB 28754 (1946).
3. ibid., PB 79578, BIOS Final Report 1151 (1946).
4. Flett, L., Soap and Sanitary Chemicals, 28, 3 (1952), pp. 36-39.
5. French Patent 953,774 I. G. Farbenindustrie to Badische Anilin and Sodafabrik.
6. General Chemical Division, Allied Chemical and Dye Corp., Tech. Bulletin SF-3.
7. Gilbert, E. E., and Jones, E. P., Ind. Eng. Chem. 43, 2022-2052 (1951).
8. Groggins, P. H., "Unit Processes in Organic Synthesis," Third Edition, New York, McGraw-Hill Book Co. (1947).
9. Grubb, H. M., and Tucker, E. B., to Standard Oil Co. of Indiana, U. S. Patent 2,374,193 (1945).
10. Kastens, M. L., and Peddicord, H., Ind. Eng. Chem., 41, 3, 438-446 (1949).
11. Kenyon, R. L., and Boehmer, N., Ind. Eng. Chem., 42, 8, 1446-55 (1950).
12. Lick, G. F., Ind. Eng. Chem., 42, 1746-60 (1950).
13. ibid., 41, 1923-34 (1949).
14. Muncie, F. W., to Colgate-Palmolive-Peet Co., U. S. Patent 2,242,-979 (1941).
15. N. V. Vereenigie Fabricken Van Stearine, Kaarsen, en Chemische Producten, Dutch Patent 27274.
16. Oronite Chemical Co., "Alkane Technical Bulletin," 20 pp. (1950).
17. Partisch, K. J. A., Fraser and Fraser Ltd., British Patent 553,-212 (1943).
18. ibid., 553,589 (1943).
19. Reed, C. F., U. S. Patents Re 20968; 2,174,110; 2,263,312.
20. Schwartz, A. M., and Perry, J. W., "Surface Active Agents," New York, Interscience Publishers Inc., 1949, pp. 47-68.
21. Suter, C. M., to Procter and Gamble, U. S. Patent 2,135,358.