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"Instantaneous" Sulfation of Fatty Alcohols[1]

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ALKYL SULFATES have been a major component in a number of detergent products for a good many years. During this time changing products and specifications have resulted in numerous changes in the materials handled and in methods of processing. However the basic problem, conversion of fatty alcohols to alkyl sulfates, has remained relatively unchanged; different solutions are required as changing conditions demand.

Basic Considerations

Conversion of a fatty alcohol to the corresponding sodium alkyl sulfate proceeds in two steps: sulfation, then neutralization. The first step is the more critical.

While sulfation can be affected with any of a great variety of different sulfating agents (1, 2, 3, 6), varying in their potency from mild to vigorous, the more common materials are limited to those in the "vigorous" category. Consequently the possibility of the occurrence of undesirable side reactions must be considered.

Usually some form of sulfuric acid, containing more or less water, is used. Consequently a considerable excess is required to displace the equilibrium to a reasonable degree of conversion. The desired reaction is, of course, the formation of the monoalkyl sulfuric acid ester.

Side reactions that may occur (5) include:

a) dehydration of one molecule to the olefin,
b) elimination of water between two molecules to give the ether,
c) oxidation to the aldehyde followed by further oxidation to the acid, and
d) esterification of this acid with fatty alcohol.

Other side reactions are possible, of course, involving isomerization, chain cleavage, carbonization, etc., resulting primarily from insufficient mixing at the point of acid addition. The first group of reactions is favored by excessive reaction times or temperatures, especially when an excess of sulfating medium has been employed. This suggests that the side reactions result from the action of acid on the alkyl sulfuric ester that is first formed.

Under normal conditions these side reactions are limited in extent, and the major consideration is the obtaining of a maximum conversion of the alcohol to the sulfate.

Early work with low molecular weight alcohols (5) has indicated that only the mono alkyl ester is formed, regardless of whether an excess of alcohol or of acid is present. Our experience with fatty alcohols strongly suggests however that these higher molecular weight materials when present in excess, as in a batch sulfation for example, form the dialkyl ester. This breaks down upon the addition of more acid to yield the mono ester.

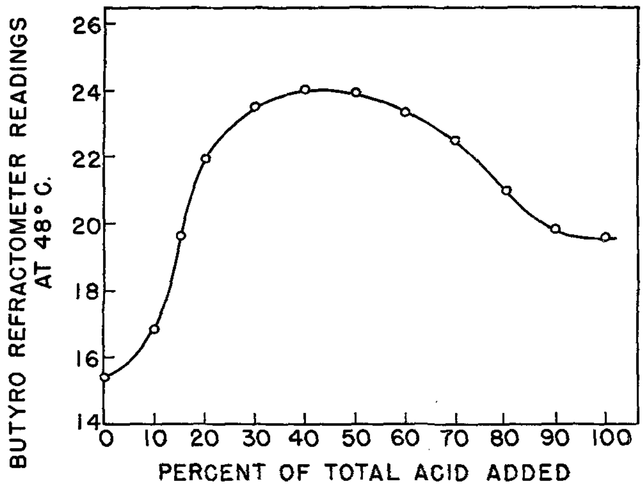

FIG. 1. Effect of Acid Usage on Refractive Index.

Confirmatory evidence for this hypothesis is shown in Figures 1 and 2. These data were obtained during batch sulfation with an equimolar usage of chlorosulfonic acid.

In Figure 1 the maximum refractive index occurs when about half the theoretical acid has been added. indicating a maximum in the average molecular weight. The actual maximum occurs appreciably before the half-way point, probably because both reactions take place concurrently once an initial concentration of the monoester has been built up.

Figure 2 is even more interesting. Sixty per cent of the total reaction heat is evolved when only 20% of the acid has been added; by the time 30% of the acid has been added, the rate of heat evolution has fallen to a rather low value. This can be explained by postulating a low heat of reaction for the conversion of the diester to the monoester. This heat distribution is of importance in the batch sulfation of alcohols with chlorosulfonic acid, the process used almost exclusively during the early days of synthetic detergent production.

Given a fixed heat exchange capacity, the initial high heat load results in a lower permissible acid addition rate during the first portion of the reaction than would have been calculated, using the over-all heat of reaction.

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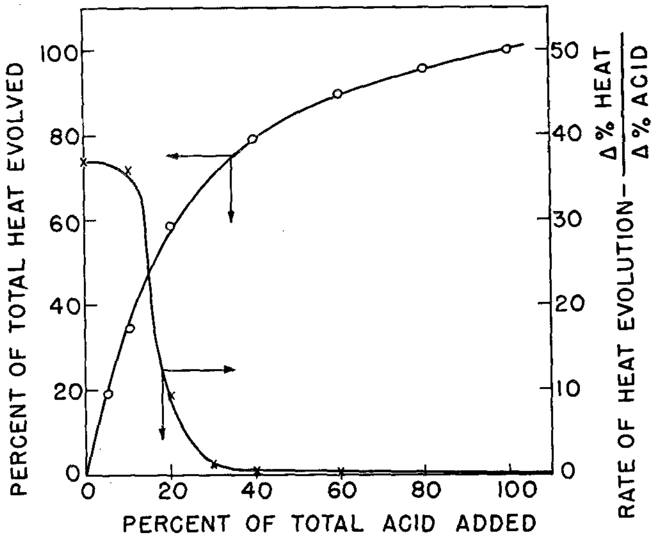

FIG. 2. Effect of Acid Usage on Heat Evolution.

The lost time cannot be made up during the second part of the reaction since during this period the acid addition rate is usually controlled by foaming of the reaction mix.

Process Development

As the technology and marketing potential of synthetic detergents improved, the batch chlorosulfonic process became increasingly inadequate. Because of the inherently long batch cycle time a considerable capital outlay would be required for production to keep up with increasing sales.

Formulation changes called for the use of increasing amounts of sodium sulfate. This was accomplished by adding powdered Na_2SO_4 before spray drying. The presence of increased amounts of comparatively coarse crystalline material in the mix led, in turn, to greatly accelerated pump wear and higher maintenance costs. Finally the disposal of by-product HCl became a progressively more difficult problem.

It became imperative therefore to develop a new process, preferably continuous and preferably employing concentrated or fuming sulfuric acid as the sulfating agent. Attempts to sulfate with H_2SO_4 batchwise were unsuccessful because of the instability of the sulfuric ester in the presence of the excess acid that is required to obtain a reasonable reaction completeness.

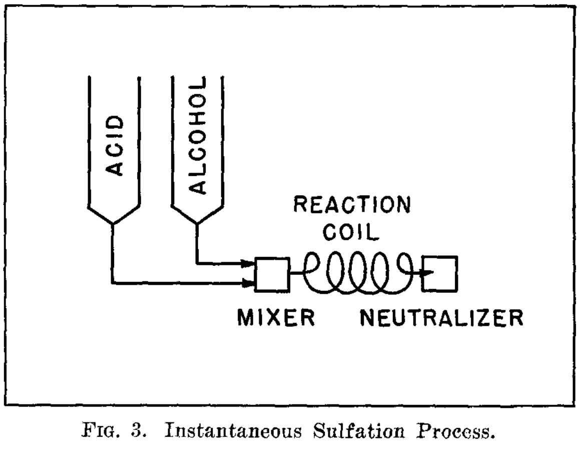

FIG. 3. Instantaneous Sulfation Process.

The first continuous runs were patterned after the batch reaction; *i.e.*, the acid and alcohol in the desired proportions were mixed, held for a predetermined reaction time, and neutralized. It quickly became evident that little could be done to limit the reaction temperature to anything even close to that normal for batch chlorosulfonic sulfations. The heat of reaction is about 150 BTU/lb. of alcohol reacting, and the reaction rate is such that while passage of the reacting mix through a cooler resulted in a reasonable exit temperature, the temperature still "ran away" in the first portion of the cooler. The end-result was a badly over-sulfated product.

The next approach was the mixing of the stock and acid followed by passage of the mix through a reaction volume such that times of 60 seconds or less could be obtained (4). No attempt was made to control the reaction temperature. Figure 3 shows a schematic diagram of the process, called "Instantaneous" or "Flash" sulfation in order to emphasize the short reaction time used. The success of this method of sulfation depends upon the fact that the desired mono-alkyl sulfuric ester is the first reaction product and that the side reaction products previously indicated are actually degradation products of the ester. By terminating the reaction, by neutralization, in just a few seconds, these secondary reactions are minimized.

Figures 4-6 show how the sulfation completeness varies with the variables of acid strength, acid usage, temperature, and reaction time.

Sulfation completeness is normally determined from the analysis for total active and the petroleum ether extract. The secondary reaction products are soluble in petroleum ether as is any unsulfated fatty alcohol. Ordinarily no effort is made to determine the relative amounts of oversulfated and undersulfated materials in the extract. Obviously, then, the drop in completeness after the maximum, as shown in these plots, is due to increasing concentrations of these secondary reaction products.

Notice that in Figure 4 both 96% and 100% H_2SO_4 will give comparable results but that, when using the latter, the reaction is much more sensitive to acid usage above the points of maximum completeness. This also appears to be true of acid usages below the optimum, but here the longer reaction time used with the weaker acid gives considerably higher complete-

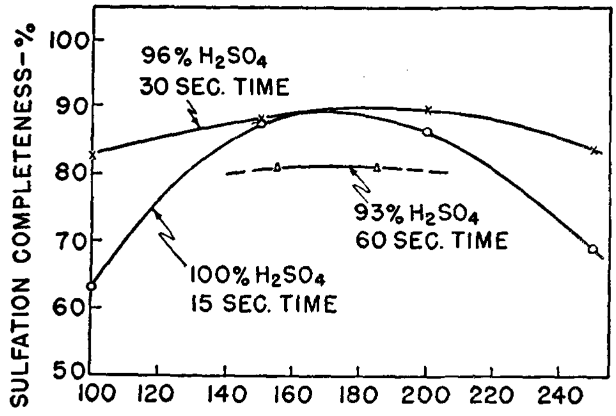

FIG. 4. Effect of Acid Usage and Strength.

nesses than would result at a 15-second reaction time. The 93% H_2SO_4 curve is surprisingly low. Apparently the reaction time is such that the secondary reaction products are present in significant amounts, even at low acid usages.

The effect of reaction time is illustrated in Figure 5. The usages of 170% and 178% of theoretical acid were designed to give about the same ratios of active to sodium sulfate in the neutralized pastes. Again, a greater tolerance for the lower strength acid is noted. An important observation is that the higher strength acid will give a higher completeness than the lower strength acid under the proper conditions. This follows from the fact that sulfation is an equilibrium reaction. Obviously, then, the potential completeness, for a given molar ratio of SO_3 to alcohol, will increase as the acid strength increases and the amount of water present decreases. To realize a gain from this increased potential requires closer and closer control of the process as acid strength is raised. As Figure 6 shows, temperature is as important as time in obtaining a high completeness. In the factory the alcohol and acid were precooled, controlling the maximum sulfation temperature at about 160°F.

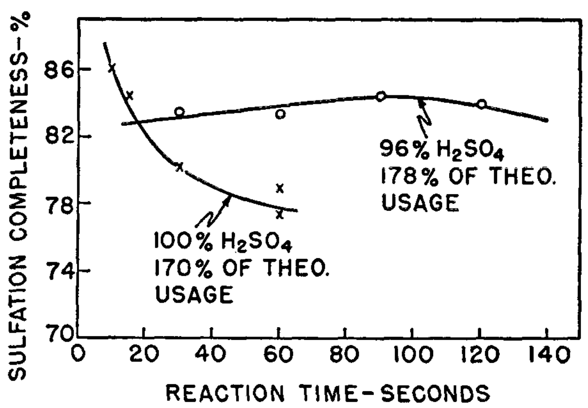

FIG. 5. Effect of Reaction Time.

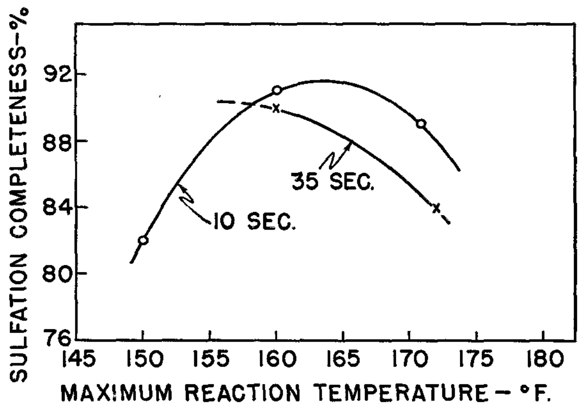

FIG. 6. Effect of Reaction Temperature.

The maximum strength acid that can be satisfactorily used in plant operation is 99% H_2SO_4. One hundred % acid would be more desirable were it not for the sharp peaking in corrosion occurring at about 100% concentration. Acids in the oleum range cannot be used in this process because of charring. This results from a combination of factors. First, the oxidizing potential of the oleums are higher than for sulfuric acid. Second, the heat of reaction of oleum and alcohol is higher than that of sulfuric acid and alcohol. Third, as acid strength is increased into the oleum range, less is required. Therefore less mass is present to absorb the heat of sulfation, and the temperature can no longer be held to a value that will give a usable product.

Neutralization

Irrespective of how well the sulfation step has been carried out, the acid mix must first be neutralized before it can be used. A poor job of neutralization can nullify much of the effort that has been expended to achieve a good sulfation.

The heat load during neutralization is considerably higher than that during sulfation and can result in temperatures well above the boiling point of water. Attempts to use a continuous process similar to flash sulfation failed due to the higher temperatures developed, which led to steam puffing and poor mixing of the acid mix and the alkali. As has been pointed out previously, sulfation is a reversible reaction, and if the mixing during neutralization is poor, local zones of low pH will develop which can lead to considerable hydrolysis, especially at higher temperatures.

The order of magnitude of this hydrolysis loss was shown by splitting a quantity of acid mix into two parts. One part was neutralized with good agitation, the other with poor agitation. The first sample showed a 90% completeness, the sample made with poor agitation dropped to 79%. Table I shows the effects of temperature and acid strength on batch neutralization in which the agitation is what might be termed fair.

TABLE I

Effect of Acid Strength and Neutralization Temperature on Completeness

% Acid	Final Neut. Temp. °F.	% Comp.
100	159	88
	173	80
96	181	86
	190	80

A process of neutralization was developed which employed a circulating system made up of a pump, a heat exchanger, and connecting piping. The pump served the dual purpose of circulating a large volume of neutralized paste and acting as a mixer to blend the streams of acid mix and caustic into the paste stream. The comparatively large volume of circulating mix dilutes the fresh paste made and prevents local high temperatures by virtue of the sheer mass of material present. Also the large volume of paste permits good velocities through the heat exchanger and therefore good heat transfer.

A large number of comparisons was made of completenesses obtained in the factory by this process and by neutralizing on a laboratory scale with dilute lye and ice. The use of dilute caustic kept the paste viscosity low and ensured good agitation. The laboratory neutralized samples analyzed almost 3% higher in completeness than obtained by factory neutralization, indicating that mixing in the factory unit was still inadequate.

An additional mixer was designed and inserted in the circulating system. The circulating paste passing through the mixer and the injected acid mix were subjected to intensive mixing action. Completenesses obtained in the factory with the neutralizer added to the system were equal to those obtained with the best laboratory techniques.

Conclusions

A continuous process has been developed for sulfating fatty alcohols with sulfuric acid up to 100% H_2SO_4 concentration.

The success of the process depends on maintaining a proper balance among the factors of temperature, reaction time, acid strength, and acid usage.

In general, best results accrue from use of as strong acid as is permissible (99% in plant operations), about 160°F. and 10 seconds reaction time.

Neutralization is quite simple, requiring only efficient mixing and adequate heat removal.

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Solubility of Tristearin and Hydrogenated Cottonseed Oil in Certain Aceto- and Butyroglycerides[1]

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THE SOLUBILITY of hard fats in liquid oils is a property of importance in the formulation of commercial fat products like shortening and margarine oil. In such products the proportion of fat crystals which dissolves in the oil or liquid phase over a given temperature range has a decided influence on the consistency of the product. It is recognized, of course, that crystal size and shape and mode of deposition also are important factors, but they are outside the scope of the present discussion.

Solubilities of hard fats in some of the more common liquid oils have been determined by Hofgaard (2), Kraemer and Bailey (5), and Craig *et al.* (1). Possibly others have published data which included isolated determinations of solubility. There appears to be no published information on systems containing aceto-oleins or butyro-oleins.

In the course of earlier work by two of the present investigators (4) it was discovered that the consistency of mixtures of an aceto-olein product and hard fat did not undergo as marked a change with a change in temperature as did the consistency of a mixture of the same hard fat in liquid soybean or similar oil. Some of the mixtures containing an aceto-olein product possessed an almost constant consistency over the temperature range of —15 to 50°C.

The present investigation was undertaken to establish the role of solubility in the consistency of fat mixtures containing acetoglycerides and to obtain fundamental information which could be used in the development of new fat products. The solubility of tristearin and hydrogenated cottonseed oils (iodine values, 1.1 and 29.3) in binary mixtures with aceto-oleins and other liquid fats was measured by the so-called "synthetic method" of Harwood, Ralston, and Selby (3).

Experimental

Materials. The samples of 1,2-diaceto-3-olein and 1,2-dibutyro-3-olein were prepared by a procedure essentially as described by Feuge *et al.* (4). Purified methyl oleate was converted to 1-mono-olein by interesterification, molecular distillation, and fractional crystallization from acetone. The 1-mono-olein (purity about 98%) was mixed with chloroform and pyridine and allowed to react with a slight excess of acetyl or butyryl chloride in chloroform solution. The reaction product in each case was purified by washing with dilute acid and water, bleaching with clay and carbon, and repeated fractional crystallization from commercial hexane. The purified 1,2-diaceto-3-olein had a melting point of —18.3°C., an iodine value of 57.5 (theoretical, 57.6), and a hydroxyl value of 0. The purified 1,2-dibutyro-3-olein had an iodine value of 51.3 (theoretical, 51.1), and a hydroxyl value of 0.

The aceto-olein product which was used was the same as that described previously (4). For its preparation commercial oleic acid was purified to yield a fraction containing about 97% of oleic and iso-oleic acids. This fraction was converted into a glycerol-free, technical grade monoglyceride (62.5% of monoesters) and acetylated with acetic anhydride. The reaction product obtained was washed with water, bleached with clay and carbon, and steam-deodorized. The final product had a melting point of —24.0°C., an iodine value of 63.9, and a hydroxyl value of 6.8.

Triolein was prepared from purified methyl oleate by letting it react with glycerol in the presence of lithium hydroxide and then purifying the reaction product (4). The triolein had a melting point of 5.0°C., and iodine value of 85.3, and a hydroxyl value of 4.9.

The tristearin was prepared by esterifying stearic acid (purity better than 99%) with glycerol, using stannous chloride as a catalyst. The reaction product was first washed with dilute hydrochloric acid, then with a solution of sodium carbonate, and then purified by fractional crystallizations from hexane and absolute ethanol. The final product had a hydroxyl value of 2 and a melting point of 72.3°C. (generally accepted melting point, 72.5°C.).

The cottonseed oil used was a commercial, alkali-refined and bleached oil having an iodine value of

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