The Sulfonation of Castor Oil With Sulfur Trioxide

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ABSTRACT

Castor oil can be sulfonated directly with SO_3 in commercially available continuous and batch equipment. The product has good color, excellent water solubility and improved acid stability. The process has the following advantages. It is more direct and considerably faster than the present process. It requires fewer man hours and, therefore, is more economical. Conditions can be varied to give a wide range of products having different solubility characteristics and combined SO_3 content. Since the reaction, batch or continuous, is stoichiometric, no waste products are formed, thus eliminating any pollution problems.

INTRODUCTION

Sulfonated castor oil, better known as Turkey red oil, is probably the oldest nonsoap surfactant which is still in use today. It was first introduced as a textile adjunct (dyeing assist) in 1875 (1). From the time of its commercial introduction the product has traditionally been prepared by the gradual addition of cold H_2SO_4 to the stirred oil. The process requires from 20-30 hr for completion and the resulting product is essentially sulfated, rather than sulfonated castor oil. While reaction conditions and methods of neutralization have been varied, and additives have been used to increase the amount of organically combined SO_3, all previous commercial production methods have been sufficiently similar that all the various end products have substantially the same performance characteristics.

As part of a continuing program to develop improved sulfonation technology, we have studied the variables involved in the sulfonation of castor oil with stabilized SO_3. The following factors have been determined to be of prime significance in producing a salable product: Light color, complete water solubility, improved acid stability, and an economical procedure.

Light color is basically an esthetic property. When offering an improved product to the trade, it should have a color at least comparable to the one in current use. Good water solubility is imperative if the product is to function efficiently as an emulsifying agent or a textile surfactant. Acid stability is desirable when preparing emulsions of acidic salts where surface activity is required under acidic conditions. The fourth factor speaks for itself.

EXPERIMENTAL PROCEDURES

Laboratory Study

Laboratory work, using SO_3 vapor diluted with air, indicated that it was possible to produce a true sulfonated castor oil possessing desired properties in 20-25 min as opposed to the 20-30 hr required with sulfuric acid. This eliminated the long hours of digestion, settling and removal of wash liquors. Also, since no water is formed during the reaction with SO_3, no excess acid is required to maintain acid strength sufficiently high to allow the reaction to proceed to completion.

Hydrolysis tests have shown that castor oil treated with SO_3 is much more stable when refluxed, under acidic conditions, than castor oil sulfated with sulfuric acid. This would indicate that a higher degree of actual sulfonation, i.e., direct carbon-sulfur bonding takes place when the SO_3 is the sulfonating agent.

Theoretically, it is possible to react up to six moles of SO_3 with one mole of castor oil. Glyceryl ricinoleate, the major component of castor oil, contains three double bonds and three hydroxyl groups, each reactive site capable of reacting with one mole of SO_3. In the original laboratory work, a molar ratio greater than 3:1 usually resulted in a sticky mass resembling synthetic rubber. In the laboratory, the best ratio appears to be about 2:1, i.e., two moles of SO_3 to one mole of castor oil.

In a typical laboratory batch reaction, castor oil is charged to a reaction flask and SO_3 diluted to 4%, by volume, with dry air is introduced below the surface, while agitating vigorously. The reaction temperature is maintained between 45-50 C and the reaction time is between 20-25 min. After all of the SO_3 has been added, the reaction mass is drowned in 15% sodium hydroxide. The resulting product has a color comparable to material prepared from sulfuric acid, contains about 25% water, and has 8% organically combined SO_3, based on 100% solids. It also displays excellent water solubility at all concentrations.

Pilot Plant Study

Having made a successful product by a batch reaction in the laboratory, work was begun in the pilot plant, using the Allied continuous sulfonation reactor.

The objectives of the pilot plant work were to: (a) duplicate the color and water solubility of the product produced in the laboratory; (b) produce a product with superior acid stability; and (c) to demonstrate that this reaction can be successfully performed in available commercial equipment.

Results obtained in the laboratory sulfations (sulfonations) can generally be duplicated in the pilot plant, and product quality is often improved because of better heat removal and SO_3 distribution in the continuous reactor.

Conditions established in the laboratory are generally transferable to the pilot plant reactor. However, since contact between the SO_3 and castor oil is more intimate in the continuous system, the conditions of the laboratory work were taken only as a starting point. Conditions were then varied around this point to determine whether more or less severe treatment of the oil would produce a more stable or otherwise more disirable product.

During laboratory experimentation a reaction temperature of 45-50 C was found to be optimum, because the reaction mass became too viscous below 45 C to allow efficient agitation and above 50 C, the color degraded and some oxidation began to take place, as evidenced by the release of SO_2. The design of the continuous reactor and reaction conditions make it very difficult to get a true reading of the reaction temperature. In a batch system, the so-called reaction temperature is actually the temperature of the reaction mass and not the true temperature of reaction. In the continuous reactor, there is no reaction mass as the organic film coming in contact with the SO_3 is only about 0.0015 in. thick. For this reason, the cooling water temperature is used as a reaction condition in place of the mass temperature.

RESULTS

During the first four runs, the SO_3 castor oil ratio was held constant, at 2:1 moles and the temperature of the cooling water was varied. Table I shows the effect of

TABLE I

Constant Molar Ratio, SO_3/Castor Oil, 2:1

Sample	Cooling water	Combined SO_3, % Before hydrolysis	Combined SO_3, % After hydrolysis	Sulfate-sulfonate ratio	Per cent hydrolyzed
1[a]	50-55	---	---	---	---
2	65-70	8.6	2.7	3.2/1	68.5
3	73-79	9.0	2.7	3.3/1	70.0
4	85-90	7.8	2.0	3.9/1	74.5
5[b]	90	4.4	1.8	2.5/1	58.0

[a] Neutralized product—not water soluble.

[b] Molar ratio SO_3/castor oil, 2.3:1.

varying cooling water temperature employed for each run. The maximum amount of combined SO_3 was obtained when cooling water temperature was held within the 73-79 C range.

A fifth run was made at a temperature of 90 C and the molar ratio of SO_3/castor oil was increased to 2.3:1. The product of run number 5 contained a somewhat lower total combined SO_3, and had a considerably lower sulfate-sulfonate ratio (greater proportion of sulfonate).

The increased temperature induced side reactions, including oxidation, which reduced the total amount of SO_3 available for sulfonation, thereby reducing overall yield.

Based on these observations, three more runs were made holding the cooling water temperature constant at 75 C (apparent optimum temperature) and increasing the SO_3/castor oil ratio. The results of these runs are shown in Table II. Products of runs 6, 7 and 8 all contain approximately 9% combined SO_3. Proportion of sulfonate increased with increase in SO_3 ratio.

DISCUSSION

After 2 hr of acid hydrolysis, a degree sufficient to completely hydrolyze the oxygen-sulfur bond, the picture changes. As suggested in the first set of runs, the sulfate-sulfonate ratio decreases directly with an increase in the SO_3/castor oil ratio. After the acid hydrolysis, the product of run 6 was 82.5% hydrolyzed, the product of run 7 was 72.6% hydrolyzed, and the product of run 8, which had an SO_3/castor oil ratio of 2.75:1, was only 34.5% hydrolyzed. The remaining acid stable material in each run is a true sulfonate. This data clearly indicates that a superior product can be made when sulfonating with SO_3 in a thin film continuous reactor.

In addition to the fact that a more acid stable product can be made by treating castor oil with SO_3 in a continuous system, there are economic advantages in using SO_3.

1. It is a direct method. The castor oil and SO_3 are metered into the reactor and the acid reaction product can be immediately neutralized to yield any solids strength desired, depending only on the choice of base and degree of dilution used. (Any desired salt may be prepared depending on selection of the base used to neutralize the reaction product.)

2. By changing the cooling water temperature or the SO_3/castor oil ratio, any of a variety of products can be made with respect to combined SO_3, acid stability or water solubility, tailored to end use requirements.

3. Since the reaction is essentially an addition reaction, everything that goes into the reactor or neutralization system ends up as active product. This eliminates wash liquor disposal which contributes to the growing pollution problem.

Continuous Reactor

The reactor used for this work was the Allied Chemical continuous sulfonation unit. Figure 1 is a vertical cross section of the reactor. Essentially, the reactor consists of a set of vertically mounted, water jacketed, stainless steel, concentric cylinders, and is divided into three distinct sections: the distribution section, the reaction section, and the separation section.

The main function of the distribution section is to direct flow so as to deposit, continuously, an even film of organic to the inner and outer walls of the reaction section. This is accomplished by pumping the castor oil through small peripheral slots in the distributor.

The SO_3/air mixture is introduced above the distributor and passes through the annular space between the concentric cylinders in such a way that contact is made with the castor oil, just at the point where the film is developed.

In the upper part of the reaction section, the gas stream containing the initial concentration of SO_3 contacts the unreacted castor oil. As the gas stream and the organic film continue to move together down the reactor walls, SO_3 is absorbed by the liquid organic phase, reacting with it so that at the end of the reaction section SO_3 remaining in the gas phase approaches zero concentration. Virtually all the SO_3 in the entering gas stream is absorbed by the organic film and converted to organic sulfate or sulfonate.

The film is in intimate contact with the water jacketed reactor walls, and movement in the liquid film generated by differential velocity of the gas stream provides an efficient heat removal and thus excellent temperature control. It also minimizes localized overheating. The reaction mass then

TABLE II

Constant Cooling Water Temperature, 75 C

Sample	Cooling water	Combined SO_3, % Before hydrolysis	Combined SO_3, % After hydrolysis	Sulfate-sulfonate ratio	Per cent hydrolyzed
6	2.0/1	8.6	1.5	5.7/1	82.5
7	2.3/1	8.8	2.4	3.7/1	72.6
8	2.75/1	8.7	5.6	1.6/1	34.5
Commercial turkey red oil	---	6.2	0.3	20/1	96.0

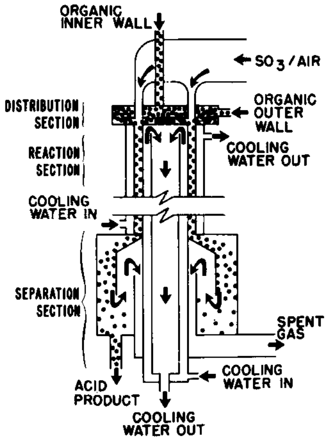

FIG. 1. Cross section of reactor.

passes into the separation section where acid product is withdrawn for subsequent processing and spent gas is separated and exhausted to atmosphere through a suitable mist filter. The direct continuous addition of SO_3 in the film reactor thus eliminates the time-consuming, slow addition of sulfuric acid required by the older methods.

Figure 2, schematically illustrates a complete sulfonation plant. The castor oil is pumped (metered) from storage to the distribution section of the reactor, previously discussed. The ratio of SO_3 to organic has been shown to be critical to the reaction, therefore, the liquid SO_3 is delivered to the vaporizer by a proportioning pump. The vaporized SO_3 is diluted with dry air from the blower to approximately 4%, by volume, and the gas mixture introduced into the reactor. Other elements of Figure 2 show the basic auxiliary equipment necessary for proper handling of feed and reactor products.

Analytical Procedures

The following analytical procedures were used to evaluate the material produced:

Combined SO_3. The combined SO_3, before and after hydrolysis, was determined by a cationic titration of the neutralized product. The sample for analysis was diluted to a concentration of 20 mg/ml. Five milliliters of this solution were then added to a graduated, stoppered cylinder containing 15 ml chloroform and 25 ml of methylene blue solution. Small increments of 0.005 N cationic surfactant Hyamine 1622 (Rohm and Haas Co.) were added, and the cylinder shaken after each addition. All of the color resides in the chloroform layer until the end point is reached, at which time the color is evenly distributed between the aqueous and solvent phase. Eighty, the molecular weight of SO_3, is incorporated in the calculation to give the actual amount of organically combined SO_3 in the anionic surfactant.

Acid Stability Tests. The acid stability tests were run by adding 10 g of the sample to 200 ml of water. This solution was then adjusted to a pH of 2 with hydrochloric acid and allowed to reflux for a period of 2 hr. The solution was then cooled and made up to 500 ml, giving a concentration of 20 mg/ml. This solution was then analyzed for combined SO_3 in the manner just described.

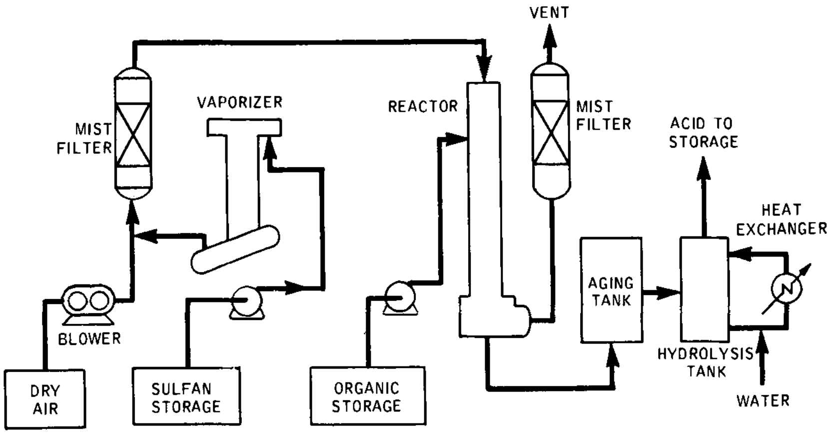

FIG. 2. Continuous sulfonation system.

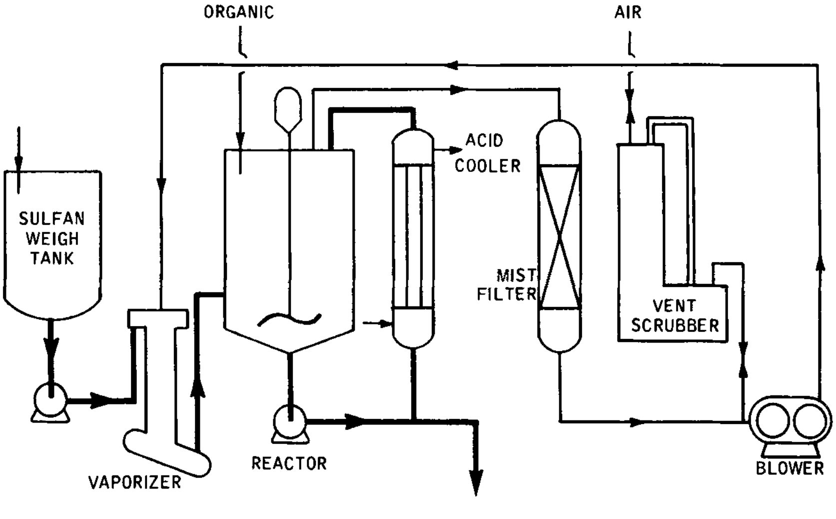

FIG. 3. Batch sulfonation system.

Comparison of Proposed and Present Methods of Sulfonating Castor Oil

To date, all of the pilot plant work has been done on continuous equipment. There is however, no good reason why this reaction could not be run in a batch reactor. Some of the inherent advantages of continuous operation would be lost, but it would certainly be an improvement over the present batch sulfuric acid procedure.

Batch Sulfuric Acid Process. About 25-30%, by weight, of 96% sulfuric acid is slowly added to the castor oil over a period of 2 hr. During this addition, the reaction temperature should not exceed 35 C. The reaction mix is agitated for another 2 hr and then allowed to stand overnight. The next step consists of washing the acid with a 10-15% solution of sodium sulfate, sodium hydroxide or sodium chloride depending upon the end product desired. The mix is again allowed to stand from 2-4 hr, for settling, after which the wash liquor is drawn off and the sulfated castor oil is neutralized and adjusted to the proper concentration. The total elapsed time is 20-30 hr.

Batch SO_3 Process. A batch SO_3/air system, on the other hand, would operate in a manner similar to that used in the continuous system, except that the continuous reactor would be replaced by a stainless steel reaction vessel, equipped with a turbine agitator, a recirculating pump and a heat exchanger. Figure 3 is a schematic of the batch SO_3/air system. The reaction principle is the same as that used in the initial laboratory work. The castor oil is charged to the reactor. The SO_3 is then vaporized, diluted with air and introduced below the surface of the castor oil at the periphery of the turbine.

During the addition of the SO_3 the reaction mass is continually pumped from the bottom of the reactor through a plate heat exchanger to maintain the proper reaction temperature, and then back to the reactor. This entire reaction can be operated as a closed system, thereby eliminating the need for air drying and exit gas filtration equipment. After the prescribed amount of SO_3 has been added, the acid is immediately neutralized with caustic to give the desired concentration in the finished product.

REFERENCE

1. Gilbert, E.E., "Sulfonation and Related Reactions," Interscience Publishers, 1965, p. 363.

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