Primary Examiner—Morris O. Wolk  
Assistant Examiner—Michael S. Marcus  
Attorney, Agent, or Firm—Louis J. Bachand  

**ABSTRACT**

Sulfonation of sulfonatable compounds such as the higher alkyl benzenes to products useful in detergent ingredient preparation, by the reaction, under intensive mixing conditions, of the sulfonatable compound and a sulfonating agent in a mass of circulating reaction mixture is improved through the use of opposed centrifugal pumps which provide through shearing turbulence the degree of vigorous mixing required in the reaction zone. In addition, spent sulfonating agent, to be used to dilute withdrawn portions of the reaction product for separation of the sulfonated product is itself first diluted by water addition to achieve a temperature and sulfonating agent concentration, prior to mixture with the reaction product, which facilitates separation of sulfonated product and sulfonating agent.

4 Claims, 2 Drawing Figures
SUMMARY OF THE INVENTION

It is a major objective of the present invention to provide improvements in the art of sulfonating sulfonatable compounds to achieve lighter colored sulfonated products more rapidly, more reliably, and more efficiently, i.e. with lower residual oils.

The invention thus provides a process for sulfonating sulfonatable compounds which includes maintaining a fluid and preferably liquid mixture of the compound, a sulfonating agent and product sulfonated compound in a circulating stream, passing the mixture to a primary reaction zone in which the mixture is subjected to vigorous agitation under sulfonating conditions and expelling the agitated mixture forcefully from the primary reaction zone under a first head, forcing the expelled mixture through a secondary reaction zone against an opposing second and lesser head generating vigorous shearing turbulence in the mixture within the secondary reaction zone, circulating the mixture from the secondary reaction zone back to the primary reaction zone as a reaction stream, cooling the stream during circulation, feeding to the primary reaction zone fresh compound and fresh sulfonating agent, withdrawing from the circulating stream a portion thereof containing product sulfonated compound, the withdrawn portion being substantially equal in volume to said feed and passing the withdrawn portion to a separation zone wherein the sulfonated compound is separated from the remainder of the withdrawn portion.

The withdrawn portion may be further treated to lower the viscosity thereof to facilitate separation of the sulfonated compound as by the addition of a diluent mixture of sulfonating agent and water to the withdrawn portion to lower its viscosity in advance of its introduction into the separating zone. The diluent has a ratio of agent to water such that the withdrawn portion when entering the separation zone has a sulfonating agent concentration between 75 and 82% by weight.

The source of the sulfonating agent may be spent sulfonating agent which has previously been separated from the withdrawn portion, which in preferred embodiments of the invention is further diluted by controlled water addition prior to introducing the sulfonating agent into the withdrawn portion.

Importantly the rate of addition of sulfonating agent to the withdrawn portion is controlled to effect the desired concentration of agent in the portion for efficient product separation with reference to the preexisting concentration in the portion as withdrawn. Moreover, assuming a rate of agent addition, the manner of water addition thereto is controlled to produce an amount of heat of solution to heat the portion to which the diluent is added to 100° to 40°F above the temperature of the reaction stream.

Thus the circulating stream is desirably maintained through cooling at a temperature between 100° and 130°F, or by control of rate of feed. The withdrawn portion is maintained preferably at a temperature above the reaction stream temperature e.g. 10° to 40° above that temperature. This temperature control may be realized through the addition of the sulfonation agent and water diluent at an appropriate temperature, as described.

The ratio of the primary reaction zone output heat is generally between 1½ and 5 and preferably about 2.
Apparatus is provided for carrying out the method comprising means for circulating a fluid reaction stream including a circulation loop and first and second pumps in opposed relation in the loop such as and preferably unequal centrifugal pumps with the first pump providing the greater output head, means feeding sulfonatable compound and means feeding sulfonating agent into the first pump to mixture there with the reaction stream, and to discharge as a reaction mixture into the second pump, the greater output head of the first pump forcing the reaction mixture through the second pump at a desired circulating rate against the opposing pumping action therein to provide shearing turbulence in the reaction mixture within the second pump, means cooling the reaction stream in the loop and means withdrawing sulfonated product containing reaction stream from the loop.

The apparatus may further include means separating sulfonated compound from other withdrawn portion components principally spent sulfonating agent such as a settling tank and means to alter the viscosity of the withdrawn portion to facilitate separation of the sulfonated compound. The viscosity altering means may include means adding sulfonating agent and water diluent to the withdrawn portion to adjust the concentration of sulfonating agent therein e.g. by returning spent sulfonating agent separated from the withdrawn portion in advance of the settling tank. Water may be added to the separated spent sulfonating agent in advance of the return of the agent to the withdrawn liquid portion by provision of means therefor in a manner to produce a mixture of water and sulfonating agent in proportions which will bring the withdrawn portion to a desired sulfonating agent concentration for separation when added thereto.

**BRIEF DESCRIPTION OF THE DRAWINGS**

FIG. 1 is a schematic flow sheet illustrative of a continuous process embodiment of the invention.

FIG. 2 is a fragmentary schematic view of an alternative form of product separation and spend acid recirculation.

**DESCRIPTION OF THE PREFERRED EMBODIMENTS**

The present process is particularly adapted to the production of sulfonated aryl hydrocarbons. The term "aryl hydrocarbon" herein refers to aromatically unsaturated compounds, preferably mononuclear, which may have none or up to two substituent hydrocarbon groups such as and preferably alkyl or alkylene groups having a total of from 1 and preferably 8 to 22 carbon atoms. Among specific compounds there may be mentioned benzene, toluene, vinyl benzene, cumene, isopropylbenzene, 2-ethylhexylbenzene, nonyl benzene, decyl benzene, undecyl benzene, dodecyl benzene, tri-decyl benzene, octadecyl benzene and eicosyl benzene. For the preparation of sulfonated aryl hydrocarbons to be used in detergent preparation it is preferred to employ alkyl benzenes in which the single alkyl substituent contains from 8 to 18 carbon atoms.

Aryl hydrocarbons are illustrative of a "sulfonatable compound" by which term is meant organic compounds which are reactive with sulfonating agents under reaction conditions of temperature and agitation which are not destructive of the compound. Typically these compounds have carbon to carbon unsaturation either aromatic or ethylenic unsaturation i.e. \( \text{>C=C<} \) groups in the compound.

In addition to aryl hydrocarbons already mentioned, other sulfonatable compounds resolvable herein include naturally occurring plant and animal esters e.g. palm oil, coconut oil, babassu oil, soybean oil, castor oil, tallow, whale and fish oils, grease and lard, olerokerite, rape seed, spermaceti, and tung oils and the like and mixtures thereof. Also there may be mentioned synthetically produced fatty acids and esters e.g. by the oxidation of petroleum, or by the hydrogenation of carbon monoxide (Fischer-Tropsch), and rosin and other resin acids e.g. tall oil.

The sulfonating agent herein comprises \( \text{H}_2\text{SO}_4 \) in aqueous solution at a concentration sufficient to sulfonate the sulfonatable compound and typically between 66\(^{\circ}\) and 71.7\(^{\circ}\) Be., the higher concentrations of course including free \( \text{SO}_3 \). Oleum which contains about 20\% free \( \text{SO}_3 \) has a Baume value of 68.4\(^{\circ}\) is the preferred sulfonating agent.

With respect to FIG. 1 and with respect to aryl hydrocarbon sulfonation as illustrative there is introduced into first pump 10 which serves as a mixing-reacting-pumping zone sulfonatable aryl hydrocarbon along line 12, sulfonating agent (oleum) along line 14 and circulating reaction stream from line 16. The first pump 10 defines a first reaction zone and is preferably a suitably sized centrifugal pump, e.g. one providing fifty pounds of output head. The reactants and reaction stream are introduced into the eye 10A of the first pump 10 to insure thorough mixing of the reactants and reaction therebetween without excessive temperature rise. Because the fresh reactants are but a minor fraction e.g. 2 to 20\% of the total liquid mass within the first pump 10, the heat rise in the mass, from the exothermic sulfonation reaction is kept small. The output of the first pump 10 is expelled with driving force from the pump along line 18 to second pump 20, also a centrifugal pump or other nonpositive displacement pump, the function of which is to strenuously agitate, with shearing turbulence the first pump output, as will be explained hereinafter.

Typically liquid, the reaction stream passing through the pump 20 enters line 22 still under pressure from first pump 10 to give circulating impetus thereto. Cooler 24, a heat exchanger, is provided to cool the reaction stream entering the cooler from line 22 to a suitable temperature e.g. 100\(^{\circ}\) to 130\(^{\circ}\)F, which is a preferred reaction temperature range for good product color with high reaction efficiency. From cooler 24, the reaction stream passes along line 26 to a tee 28 which passes one portion of the reaction stream to line 30 for circulation back to the first pump 10 and a second portion of the reaction stream to line 32 for product separating treatment (to be described) in a manner controlled by valve 48 on product line 46. From line 30 the reaction stream enters a holding tank 34 which is suitably agitated to insure temperature uniformity and good reactant contact. After a suitable residence time e.g. 1 to 75 minutes, the reaction stream is passed out of the tank 34 along line 16 for circulation back to the first pump 10.

While the circulation loop just described to comprise first pump 10, line 18, second pump 20, line 22, cooler 24, line 26, line 30, holding tank 34 and line 16 is depicted as a continuous unit, batch operation is feasible by premixing the reactants from line 12 ad line 14 in a
a critical step in the present process is the achieving of turbulence in the second pump 20 which provides the vigorous shearing mixing of reagents in the secondary reaction zone defined by this pump with the stream mass in a manner to essentially complete the sulfonation reaction to minimize residual oil and withal limit heat rise to a level at which product color development is unobjectionable. To do this, the present process employs an oppositely acting pump operating against the first pump determined prevailing flow of the reaction mixture. In terms of equipment these flows are obtained by juxtaposition of oppositely acting pumps, the first one having a far greater output head than the other, e.g. between 1/4 and 3 times as great. Thus first pump 10 delivers its output centrifugally through line 18 forcefully into second pump 20. Pump 20 is connected in the system with its outlet to the line 18 whereby the stream is forced backward through this pump i.e. centrifugally, against its pumping element which exerts a nominal output head e.g. 30 pounds so that the net head in line 22 where pump 10 has an output head of 50 pounds is 20 pounds. The opposed pumps 10 and 20 are set at a distance such that the output of pump 10 produces agitating turbulence within pump 20 through the churning of the pumping element against the countervailing flow of the reaction stream.

As stated, a portion of the recirculating reaction stream is passed through tee 28 out of the circulating loop to line 32. This withdrawn portion is equal in volume to the combined volumes of feed entering at the pump inlet 10a. Liquid in line 32 is drawn into the inlet of a third pump, pump 36, which conveniently may be a centrifugal pump also, or any other form of pump. The pump 36 pumps the withdrawn portion out along line 40 to a separation zone here shown in the form of a settling tank 42. Within the settling tank 42, in a known manner not needed to be detailed here, but which is indicated by the dotted lines 44, the withdrawn portion separates from a mixture of phases into an upper phase comprising essentially sulfonated aryl hydrocarbon and a lower phase comprising essentially water and sulfonating agent. The upper layer is drawn off along line 46 through back pressure valve 48 to storage or other processing such as neutralization. The lower layer is drawn off from tank 42 along line 50 into a cooling loop comprised of line 52, pump 54, line 56, cooler 58, and line 60 and return line 62. A portion of cooled material is taken to storage in tank 64 along line 66 through valve 68. From storage tank 64 the spent sulfonating agent may be drawn along line 70 to reuse at pump 36.

The lower layer in tank 42 as mentioned contains sulfonating agent and water. The proportions of these is such that the mixture is not of sulfonating strength. The mixture is thus referred to as “spent” sulfonating agent. It is known to use this spent sulfonating agent to condition the sulfonation product-containing withdrawn portion in line 32 to facilitate subsequent separation operations. As obtained in line 32 the reaction product is an intimate liquid admixture of substantial viscosity which resists rapidly separating into distinct phases. It has been determined that lower viscosities through dilution and/or higher temperatures will assist in rapid phase separation. In the past, spent sulfuric acid as separated has been used as a diluent to lower viscosity prior to attempting separation.

In the present process with reference to FIG. 1, the sulfonating agent separated from settling tank 42 along line 52 as in previous processes typically contains about 80% by weight H₂SO₄, the balance being essentially water. This agent content is more or less dictated by good separation practice considerations. The sulfonating agent in the withdrawn portion (line 32) usually will contain about 90% by weight H₂SO₄ which is too high for effective separation. Merely mixing the 80% H₂SO₄ spent sulfonating agent from tank 42 returned along line 70 with the 90% H₂SO₄ agent entering the pump 36 from line 32 as has been the practice in the past does not easily result in a readily separable mixture. This is because easiest and most rapid separation in tank 42 occurs when the agent contains between 75 and 82% H₂SO₄.

In this process the problem just described is avoided by modifying the spent sulfonating agent obtained from the settling tank to have a lower H₂SO₄ content, one proportioned to the sulfonating agent H₂SO₄ concentration in the withdrawn portion on the one hand and to the H₂SO₄ concentration desired in the sulfonation agent in the settling tank. In FIG. 1, the spent sulfonating agent is modified by dilution through water addition to the agent in line 70 from water addition line 72 controlled by valve 74 which is adjusted for more or less water flow with regard to H₂SO₄ concentration in the sulfonating agent flowing in line 70, its concentration in the agent in the withdrawn portion in line 32 and its desired concentration in line 52.

Water addition as described produces a heat of solution greater or less depending on proportions, rate and manner of addition of the water. It has been found that this heat of solution may be used to advantage in the present process. Separation of the product and reagent phases in tank 42 is temperature dependent. Temperatures in the settling tank 42 above those optimum for reaction and particularly 16°F to 40°F above the reaction stream temperature have been found to improve the rate of separation in the tank. The spent sulfonating agent exiting from tank 42 is cooled in the cooling loop having cooler 50°F to about 70°F typically, to reduce the possibility of damage to the piping and equipment. This temperature may be raised by the addition of water from line 72 as the sulfonating agent is passed from storage 64 along line 70 to pump 36, and the heat added to the withdrawn portion.

In FIG. 2, the apparatus for separating the product sulfonated hydrocarbon and spent sulfonating agent comprises a settling tank 421, having a product outflow line 461 with back pressure valve 481 and a spent agent outflow line 521. In addition, in this embodiment there is provided a spent agent circulation and mixing loop 74 comprising a pipe 77 having a valve 78 controlling flow from tank 421. A venturi section 80 in pipe 77 is provided downstream of valve 78 for receiving and mixing withdrawn portion from line 32 and under positive pumping pressure with spent sulfonating agent from tank 421. The forceful introduction of the withdrawn portion into the throat of the venturi section 80 induces a flow of spent sulfonating agent from tank 421 into the loop 74 in a ratio proportionated between withdrawn portion and spent agent dependent on the proximity of the end 32a of the line 32 to the venturi section 80, with greater spacing inducing a less flow of spent
agent and consequently a lower dilution of the withdrawn portion. Intimate mixing of the flows occurs within the venturi section 80. The valve 78 in the loop is used to control flow from the settling tank 421 independently of the induction. Loop 74 is shown to be externally fitted to tank 421 but may be entirely within the tank. The withdrawn portion feed line 32 then entering through the wall of the tank.

The loop 74 thus functions to produce the mixing of spent sulfonating agent and withdrawn portion to concentrations desirable for phase inversion and separative settling of spent agent and sulfonated product under pressure from the withdrawn portion. The recirculating flow being induced by jetting the withdrawn portion into spent sulfonating agent in advance of a venturi constriction through which the agent and withdrawn portion then pass in mixing flow. The mixed liquids are introduced into the tank 421 between lines 441.

In sulfonating with the process, the setting of valve 48 or 481 determines the withdrawal rate through tee 28 and line 32 assuming a predetermined feed rate and reaction stream circulation loop pressure. The removal of spent sulfonating agent is controlled through operation of valve 68 or 681 responsive to movement of float 76 or 761 maintained at the interface of the sulfonated product and sulfonating agent in tank 42 or 421. Valve 68 and float arm 76a (and valve 681 and float arm 761a) shown schematically are connected e.g. electronically or pneumatically as indicated by dotted lines 78 and 781 to open valves 68 or 681 when the interface is too high and vice versa.

1. Apparatus for sulfonation comprising means for circulating a fluid reaction stream including circulation loop means and first and second pump means in opposed relation in the loop means, each of said pump means having inlet and outlet means, said first pump means having a larger capacity than said second pump means to provide a greater output head, separate means for feeding sulfonatable compound and sulfonating agent into the inlet of said first pump means to mix with said circulating reaction stream in said first pump means, and means to discharge the thus formed reaction mixture into the outlet of said second pump means, the greater output head of said first pump means forcing the reaction mixture through the said second pump means at a desired circulating rate against the opposing pumping action therein to provide shearing turbulence in the reaction mixture within the second pump means, means downstream of said pump means for cooling the reaction stream in said loop means and means for withdrawing from said loop means a portion of said circulating reaction stream containing sulfonated product.

2. Apparatus according to claim 1 in which the ratio of output head of said first pump means to the nominal output head of said second pump means is between 1.5 and 5.

3. Apparatus according to claim 2 further including means for separating sulfonating agent from said withdrawn portion, said separating means comprising a settling tank, means returning the separated sulfonating agent from said settling tank to the withdrawn portion in advance of the settling tank and means adding water to said separated sulfonating agent at the withdrawing means in a manner to produce a mixture of water and sulfonating agent in proportions which will bring the withdrawn portion to a desired sulfonating agent concentration for separation.

4. Apparatus according to claim 3 in which each of said pump means is a centrifugal pump.