METHOD OF SULFONATION WITH SULFUR TRIOXIDE

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This invention relates to a method of effecting the sulfonation of organic compounds whereby increased yields of sulfonated products having a desirable color are obtained. More specifically, the invention concerns an improvement in the method of sulfonating organic compounds which comprises effecting the sulfonation reaction by contacting the stock charge at sulfonating conditions with sulfur trioxide introduced into the sulfonation reactor suspended and/or dissolved in an inert liquid carrying medium.

It has been generally known that certain organic compounds may be sulfonated by reacting the same at selected sulfonation conditions with sulfur trioxide as the active sulfonating agent and that such use of sulfur trioxide as a sulfonating agent provides a highly advantageous method of effecting such reactions. Because of the physical instability of the various forms of sulfur trioxide and the resulting difficulties encountered in handling the reagent, particularly because of its corrosiveness to the required apparatus involved, such as pumps, metering devices and mixing vessels, the commercial use of sulfur trioxide to effect sulfonation has been generally limited.

The present invention provides a method of introducing the sulfur trioxide into the sulfonation reactor by dissolution and/or suspension in an inert carrying medium comprising a low boiling paraffinic hydrocarbon thereby overcoming the difficulties associated with its use in the prior art.

The so-called “pick-up” procedure, as referred to herein, concerns the above method of introducing sulfur trioxide into a sulfonation reactor. By means of the present procedure, the advantages accompanying the use of sulfur trioxide as the sulfonating agent may be utilized. It is possible to utilize a commercial scale applicable to many organic compounds which have heretofore been considered too sensitive to be subjected to the vigorous sulfonating action of sulfur trioxide.

1. It is one object of the present invention to provide a process for effecting the sulfonation of sulfonatable organic compounds utilizing sulfur trioxide as the active component of the sulfonating agent, said process being adaptable to large scale production, either on a continuous or a batch type of processing procedure.

Another object of the invention is to sulfonate alkyl aromatic hydrocarbons to produce intermediate sulfonic acids for the ultimate production of detergents therefrom, in which product color and quality are mutually dependent factors, by a process in which discoloration and deterioration of the detergent properties of the product are substantially eliminated.

A further object of the invention is to produce sulfonated organic compounds by means of a sulfonating procedure in which high yields of the sulfonic acid product are obtained, calculated on the basis of the sulfonating agent consumed.

Still another object of the invention is to provide a process for the production of alkyl aromatic sulfonate detergents wherein an alkyl aromatic hydrocarbon is sulfonated and the resulting sulfonic acids is subsequently neutralized with a basic neutralizing agent to form said sulfonate detergent, effecting the sulfonation reaction under conditions such that substantially none of the alkyl groups are lost from the alkyl aromatic hydrocarbon charge and further providing for the immediate neutralization of the sulfonation reaction mixture to form the desired sulfonate detergent product without the necessity of separating the sulfonic acid from an excess of the sulfonating agent.

In one of its embodiments, the present invention concerns an improvement in the process for sulfonating a sulfonatable organic compound by contacting said compound with sulfur trioxide entrained in an inert fluid carrying medium which comprises passing said inert fluid medium selected from the inert paraffinic hydrocarbons containing not more than 8 carbon atoms per molecule into a mass of sulfur trioxide maintained in a pick-up zone at conditions selected to thereby entrain a portion of said sulfur trioxide in said inert carrying medium and thereafter mixing the inert carrying medium containing sulfur trioxide with said sulfonatable organic compound at sulfonation reaction conditions.

In its more specific aspects, the present invention relates to a process for sulfonating a sulfonatable organic compound which comprises passing a stream of liquid normal butane maintained at a pressure in excess of about 8 atmospheres and at a temperature of less than about 30° C. into a pick-up zone containing a mass of sulfur trioxide to thereby entrain a portion of the sulfur trioxide from the pick-up zone in said liquid butane, cooling the effluent thereof to a temperature of from about 0° to about 20° C. and admixing said effluent with said sulfonatable organic compound in an amount corresponding to a molar ratio of sulfur trioxide to the sulfonatable organic compound of from about 1:1 to about 3:1, refluxing the butane vaporized by the heat of
the resulting sulfonation reaction at a pressure sufficient to maintain the temperature of the reaction at from about -10° to about 20° C. and thereafter vaporizing said butane from the sulfonation reaction product.

Sulfonation reaction where speed of reaction and yield are important factors, it becomes desirable to maintain the proportion of sulfur trioxide in the sulfonating agent as high as possible consistent with the number of sulfonic acid groups to be introduced into the compound undergoing sulfonation by maintaining the sulfonation reaction mixture as nearly anhydrous as possible. We have discovered that by introducing pure sulfur trioxide (that is, in an anhydrous condition, free of sulfuric acid) into the sulfonation reactor entrained in an inert diluent or solvent, such as a liquid paraffinic hydrocarbon, the above desired conditions are maintained during the sulfonation reaction. Free sulfur trioxide is an active sulfonating agent such that substantially complete monosulfonation is obtained when approximately a molar equivalent each of sulfur trioxide and the compound undergoing sulfonation are present in the sulfonation reactor. Suitable conversions may be obtained in a reaction mixture wherein the ratio of sulfur trioxide to charging stock is as low as 1:1 to about 2:1 in those reactions in which monosulfonation is desired. The sulfonation of organic compounds with sulfur trioxide eliminates the problem of separating the sulfonic acid product from large quantities of excess sulfonating agent, generally required when the customary sulfonating agents such as sulfuric acid or the oleums are utilized. The sulfonation reaction mixture when utilizing sulfur trioxide as the sulfonating agent may thus be neutralized directly without the consumption of relatively expensive neutralizing agent to form the sulfonate salt of the neutralizing agent which is obtained more cheaply from other sources. The use of sulfur trioxide, therefore, effects a marked economy in the usual sulfonation process wherein the product sulfonic acid is desired in the form of the sulfonate salt, not only because of the reduced quantities of sulfonating agent required, but also because the amount of neutralizing agent required for forming the sulfonate salt is reduced.

It is the purpose of the present invention to provide a convenient method of introducing sulfur trioxide into a sulfonation reaction. The method comprises passing an inert fluid carrying medium into a bulk supply of sulfur trioxide maintained within a pick-up zone wherein the fluid carrying medium entrains a portion of the sulfur trioxide present in the pick-up zone and carries the same to the sulfonating reactor where the sulfur trioxide, in the presence of the carrying medium, contacts the organic compound to be sulfonated at the desired sulfonating conditions. By the use of the term "fluid carrying medium" herein, it is contemplated that either gaseous or liquid paraffinic hydrocarbons may be utilized to entrain sulfur trioxide in either the vapor or liquid or liquefied form.

When employing a liquid or liquefied normally gaseous paraffinic hydrocarbon as the fluid carrying medium, the reaction conditions, especially the temperature of the sulfonation reaction, may be controlled within close limits by adjusting the pressure above the reaction mixture such that all or a portion of the liquid carrying medium evaporates as the exothermic heat of the sulfonation reaction is liberated. Since one form or physical modification of the carrying medium herein specified may be an inert liquid, vaporizable at the relatively low temperatures utilized in typical sulfonation reactions, especially when the ambient pressure is adjusted to induce vaporization, the temperature of the reaction mixture is thereby limited to the boiling point of the carrying medium at the particular operating pressure. The sulfonation reactor may further be attached to a reflux condenser to continuously return the vaporized carrying medium during the reaction to the sulfonation zone. Alternatively, the vapors may be condensed in an auxiliary condenser and returned to the sulfur trioxide pick-up zone while additional liquid carrying medium in an amount sufficient to supply only that required to cool the reaction mixture by evaporation is supplied to the sulfonation zone. The close control of the temperature in this manner is especially advantageous when sulfonating a compound which is sensitive to heat and is especially applicable to the sulfonation of those compounds which undergo undesirable side reactions (such as aromatic hydrocarbons), or which form resinous or tarry substances at high sulfonation reaction temperatures. The introduction of the sulfur trioxide in the presence of a fluid carrying medium is advantageous in other respects in that the sulfur trioxide is, in effect, diluted with the inert fluid and therefore contacts the compound to be sulfonated gradually such that polysulfonation is obviated in those reactions where monosulfonation is desired, as in the case of producing monocyclic sulfuric acid for subsequent conversion to a monohydroxy phenol or in the case of sulfonating alkyl aromatic compounds for the production of sulfonate detergents therefrom. In the latter application of the present process, dealkylation of the alkyl aromatic charging stock is substantially eliminated by virtue of the absence of water and the gradual contact obtained between the charge and the sulfur trioxide distributed throughout an inert carrying medium. The present method eliminates the problem of dealkylation ordinarily observed when the charge is initially contacted with all or a major proportion of the sulfonating agent as, for example, when the charge is simply stirred into or otherwise mixed with the undiluted sulfonating agent.

In order to enhance the advantages of gradual contact between the charging stock and the sulfur trioxide and also to prevent polysulfonation, it is also contemplated in the present process to contact the charging stock with the sulfonating agent in step-wise batch increments accompanied by intermediate separation of the sulfonic acid product from the reaction mixture, although the desirable monosulfonation is generally obtainable without polysulfonation by the continuous method of contact when the reaction conditions are maintained within the limits herein provided. As an alternative to the intermediate separation of the sulfonic acids from the reaction mixture, the reaction rate may be lowered by use of a reactor and temperature simultaneously increasing the residence time of the compounds to be sulfonated.

Suitable charging stocks which may be sulfonated by the present procedure are herein de-
scribed broadly as sulfonatable organic compounds, although the method is particularly advantageous when applied to the sulfonation of aromatic compounds, and especially when the charge stock comprises an alkyl aromatic hydrocarbon as hereinafter specified for the formation of the corresponding sulfonic acids utilizable as detergent intermediates. Organic compounds within the broad class of charging stocks include such compounds as the phenols, and alkyl phenols; alcohols of both the aliphatic and cyclo-aliphatic series; aromatic hydrocarbons, such as benzene, naphthalene, and their alkyl derivatives such as cyclohexene and ethylenecyclohexene; heterocyclic compounds such as thiophene, pyridine and the like; ethers and esters such as phenylmethyl ether and the fatty acid glycerides respectively, the latter class including such compounds as the glyceride mono-ester of oleic acid, etc.; acids, such as benzoic acid; and amines, such as the above classes of compounds containing substituents such as one or more halo, nitro, amino, keto, carboxyl, etc. groups. The advantages of the present method of sulfonation are especially evident in the production of alkyl aromatic sulfonic acids which when neutralized with a suitable basic reagent such as an alkali metal hydroxide, an amine or an alkaline amine form highly effective detergent compounds. In the latter instance, the control of the reaction temperature is especially important and the method herein provided for effecting gradual sulfonation of the charging stock to be sulfonated permits sulfonation at a relatively low temperature, thereby eliminating the development of color bodies and dealkylation of the alkyl aromatic hydrocarbon charging stock which generally occurs when the temperature is not controlled or where the charge is contacted with all or a large proportion of the sulfonating agent. Suitable alkyl aromatic hydrocarbons sulfonatable by the present process include not only the alkylated polycyclic aromatic compounds such as naphthalene but also, and preferably, the alkyl benzeneoid hydrocarbons wherein the alkyl group contains from about 9 to about 18 carbon atoms per group, represented, for example, by dodecyltoluene.

The material herein designated as the carrying medium for the sulfur trioxide sulfonating agent is more specifically described as a paraffin hydrocarbon which is essentially inert at the temperature specified for the particular sulfonation reaction. At relatively high sulfonation temperatures, for example, at temperatures in the region of about 50° to about 100° C., it is desirable to utilize as a carrying medium for the sulfur trioxide a normally liquid inert paraffin hydrocarbon containing fewer than about 3 carbon atoms per molecule such as heptane, hexane, and pentane and paraffin hydrocarbon containing at least a portion of the inert hydrocarbon in substantially liquid phase. At relatively low sulfonating temperatures, for example, at temperatures of from about -20° to about 50° C., low boiling paraffin hydrocarbons such as propane and butane or a mixture thereof are desirably utilized as the carrying medium. The latter may be passed through the sulfur trioxide pick-up zone in either vapor or liquid condition to entrain a portion of the sulfur trioxide therein. In the subsequent sulfonation stage, the pressure therein may be increased to maintain at least a portion of the carrying medium in liquid phase.

It is generally preferred that the pick-up zone and auxiliary equipment leading to the sulfonation reactor be maintained at a temperature less than about 30° C, preferably at from about 0° to about 70° C. to avoid any reaction between the carrying medium and the sulfur trioxide. For this reason and also to provide a fluid, nonviscous medium, n-butane, propane or mixtures thereof are preferred carrying media for use in the present invention, since the latter are substantially inert and readily flow at these temperatures.

In sulfonating most organic compounds and particularly in the sulfonation of alkyl aromatic hydrocarbons where undesirable coloration of the product is likely to develop at higher sulfonation temperatures, the preferred temperature is in the range of from about -10° to about 50° C., and the preferred of the inert liquid carrying media for the reaction are the low molecular weight normal paraffin hydrocarbons. The latter inert hydrocarbons may be readily distilled from the sulfonation reaction product following the completion of the sulfonation reaction and are readily recoverable by passing the hydrocarbon vapors from the distillation through a condenser at pressures in excess of the vapor pressure of the carrying medium, although the paraffin hydrocarbon vapors may themselves be recovered and recycled to the pick-up zone, as desired.

The active component of the sulfonating agent herein utilized which provides the sulfonic acid radical attached to the sulfonatable organic compound during the sulfonation reaction is sulfur trioxide in any of its various physical modifications. Sulfur trioxide has become available commercially in three forms, the so-called α-form (a solid asbestos-like material melting at about 62° C, generally considered to be a sulfur trioxide polymer) the β-form, also a polymeric solid at normal temperatures melting at about 33° C, and the γ-form, a normally liquid modification of sulfur trioxide at room temperatures containing a large proportion of monomeric sulfur trioxide and melting at about 17° C. As previously indicated, the invention contemplates utilizing any of said forms, although the γ-form is preferred herein because of its greater adaptability to continuous processing procedures and its more desirable handling behavior. A stabilized γ-form is manufactured commercially under the trade name "Sulfan" containing an inhibitor which maintains the stabilized product in liquid condition at temperatures higher than its melting point at which temperature it would normally (in the absence of the inhibitor) be converted to the polymeric solid α- and β-forms. Sulfur trioxide has a sufficient vapor pressure that significant quantities of the vapor form may be entrained in the hydrocarbon vapor by passing said hydrocarbon vapor into the pick-up zone, even at temperatures below about 30° C.

The sulfur trioxide is for purposes of the present process maintained in a suitable tank or vessel containing a bulk supply thereof. In order to effect dissolution or entrainment of the sulfur trioxide in the carrying medium, the latter is...
allowed to percolate into the mass of sulfur trioxide to literally "pick-up" the latter and carry the same to the sulfonation reactor. In such an arrangement, pressure may be applied on the carrying medium prior to any entrainment there- in of sulfur trioxide, the carrying medium being formed through the mass of sulfur trioxide by percolation into the bottom of the vessel containing the sulfur trioxide. The inert carrying medium including entrained sulfur trioxide may then be allowed to overflow from the pick-up vessel directly into the sulfonation reactor; the flow rate being controlled by the pressure on the carrying medium flowing into the pick-up vessel. By means of this arrangement, pumps or other liquid transfer apparatus are eliminated from the effluent side of the pick-up zone to transfer the highly corrosive sulfur trioxide to the sulfonation reactor.

At equilibrium conditions, the quantity of sulfur trioxide dissolved or entrained in the carrying medium is constant at uniform temperature and contact conditions between the carrying medium and bulk supply of sulfur trioxide, such that the proportion of sulfur trioxide to sulfonatable organic compounds introduced into the sulfonation reactor may be controlled by maintaining the flow of carrying medium continuous at a predetermined constant rate. The bulk supply of sulfur trioxide in the pick-up zone may be stirred or otherwise agitated to increase the ratio of sulfur trioxide to carrying medium in the tower effluent and when desired, the stirring rate may be maintained sufficient to obtain an emul- sion of the two components. The sulfur trioxide may be deposited on carrying or spacing mate- rials such as asbestos, kieselguhr, or other fibrous or porous material having a large superficial area over which the carrying medium is allowed to flow to pick up the required amount of sulfur trioxide.

Other embodiments of the present process and the manner in which the process is operated is further described by referring to the accompanying diagram which illustrates a sulfonation procedure embodying the principles of this invention. For the sake of simplicity, the diagram will be described with reference to the sulfonation of an alkyl aromatic hydrocarbon utilizing butane in liquid form as the inert carrying medium and liquid sulfur trioxide as the sulfonating agent. It is to be emphasized in thus limiting the description to a particular charging stock and to a specific method of operation, that it is not intended to thereby limit the scope of the invention in strict accordance thereto. At other conditions of operation and utilizing other charging stocks, the procedure may be modified to effect sulfonation of any of the sulfonatable compounds hereinafter referred to.

Referring to the diagram, normal butane is introduced into the process flow through line 1, containing valve 2 and flows into line 3 containing valve 4 where the charge is commingled with recycled butane recovered as hereinbefore specified from the sulfonation reactor. The butane is compressed in pump 5 to a pressure of at least 5 atmospheres and is discharged therefrom into line 6, containing valve 7, said line 6 conveying the liquid or gaseous butane, depending upon its temperature, into heat exchanger 8 wherein the temperature is adjusted to a temperature of from about 15° to about 30° C. at which temperature the butane is substantially liquefied at pressures in excess of 5 atmospheres. Liquid butane is discharged from heat exchanger 8 into line 9 which connects with line 10, containing valve 11 for controlling the flow of liquid butane into the mass of sulfur trioxide maintained in pick-up zone 12. Zone 12 is ordinarily a lower containing sulfur trioxide in either liquid or solid form depending upon which of the α-, β- or γ- forms of sulfur trioxide are charged into said pick-up zone. For purposes of this description, pick-up zone 12 contains the liquid or γ-form of sulfur trioxide, which may be maintained in zone 12 either as a mass of liquid sulfur trioxide or deposited upon a suitable spacing material, such as kieselguhr, alumina, etc. Zone 12 is maintained at from about 18° to about 30° C. and at sufficient pressure to maintain the butane charged therein in substantially liquid phase or at lower temperatures, for operation at atmospheric pressure. The tower or pick-up zone may be fitted with a stirring device or may contain baffles or other means to effect intimate admixture of the butane with the liquid sulfur trioxide maintained therein. The effluent stream from the pick-up zone 12 is then passed through heat exchanger 13 wherein the sulfur trioxide entrained therein is directed into line 13 containing valve 14 and from line 13 into line 16.

When pick-up zone 12 becomes depleted of its content of sulfur trioxide, the flow of butane from line 9 may be directed into auxiliary pick-up zone 16 by opening valve 17 and closing valve 11, thereby directing butane from line 9 into line 18 through valve 17 into pick-up zone 16. The effluent therefrom is discharged into line 19 containing valve 20, and then into line 21. As pick-up zone 16 becomes gradually depleted of its con- tent of sulfur trioxide, by passage of butane there- through, zone 12 is recharged with additional sulfur trioxide and the butane stream diverted thereto for continuous operation.

The liquid mixture or solution of sulfur trioxide in butane comprising the effluent from the sulfur trioxide bulk supply zone is conveyed through line 16 and valve 21 into heat exchanger 22 wherein the temperature of the effluent is adjusted to the desired temperature to be maintained in the subsequent sulfonation stage of the process. The liquid mixture or solution of sulfur trioxide in an alkyl aromatic hydrocarbon charge is sulfonated to form a detergent intermediate thereby, the effluent stream is cooled to a temperature of from about 0° to about 10° C. The butane-sulfur trioxide mixture is discharged from heat exchanger 22 into line 23 through valve 24 and into sulfonation reactor 25 wherein it is thoroughly mixed with the alkyl aromatic charging stock introduced into reactor 25 through line 26 and valve 27. Sulfonation reactor 25 desirably contains a suitable mixing device such as a series of stirring paddles to effect intimate ad- mixture of the alkyl aromatic hydrocarbon charge with the butane-sulfur trioxide mixture. Since the sulfonation is normally exothermic, the heat liberated by the reaction may be dissipated by allowing the butane carrying medium to vaporize, thus controlling the temperature at the boiling point of the butane at the partial- pressure. In order to further control the reaction temperature and provide for suitable vaporization of the butane carrying medium above the reaction mixture in reactor 25 may be reduced depending upon the sulfonation temperature de- sired. The butane carrying medium vaporized during the reaction is released from sulfonation
reactor 25 through line 28 and valve 29 into condenser 30 wherein it is cooled sufficiently to liquefy the butane for recovery purposes. The liquefied butane is withdrawn from condenser 30 through line 31 and valve 32 and may be either returned in its entirety to sulfonation reactor 25, via line 33, and valve 34 or, preferably, at least a portion thereof is recycled to the initial stages of the process for picking up additional amounts of sulfur trioxide from the bulk supply zone. The liquid butane for the latter alternative operation is removed from condenser 30 through line 31 and discharged into line 35, through valve 36 into butane charging line 3 for recirculation in the process.

The sulfonation reaction product comprising alkylation aromatic sulfonic acids and usually some residual butane carrying medium, as well as excess sulfur trioxide depending upon whether a molar excess of the sulfonating agent is utilized in reactor 25, is removed from reactor 25 through line 37 and valve 38 and transferred into butane separating zone 33 wherein the butane carrying medium is vaporized from the remaining components of the sulfonation reaction mixture, usually at a somewhat lower pressure and/or higher temperature than are maintained in the sulfonation reactor 25. The vaporized gas is preferentially packed fractionating column preceded by a preheater in the incoming charge thereto may be heated prior to introducing the mixture into zone 33. Alternatively, the incoming charge may be heated by hot butane vapors from the reboiling section of the column, as hereinafter described. The relatively high volatility of butane in relation to the other components of the reaction mixture permits the butane to be readily separated from the sulfonation reaction mixture, deposition of a residue comprising predominantly alkylic aromatic sulfonic acid.

The vaporized butane is removed from separating zone 33 through line 39 and valve 40 and transferred to condenser 30 by connection of line 39 with line 29 for recycling the butane as hereinafore provided. Any residual butane which is not flashed from the mixture charged to separation zone 33 is generally removed by additional heating of the residue, for example, by contacting the latter with reboiler coil 41 in the bottom of zone 33. The residue comprising the alkylic aromatic sulfonic acid in a substantially pure state is removed from separating zone 33 through line 42 containing valve 43 to other processing apparatus, not shown, such as a neutralization zone. Because of the substantially complete conversion of the alkylic aromatic hydrocarbon to sulfonic acids thereof in the sulfonation reactor, the problem of separating unconverted charging stock is eliminated when utilizing sulfur trioxide as the sulfonating agent charged at 1:1 or slightly higher molar ratio of sulfur trioxide to charging stock.

The present invention is illustrated with respect to several of its specific embodiments in the following examples, which, however, are not to be considered as limitations of the invention in any of its broad aspects hereinafore specified.

**Example I**

In a batch apparatus for the sulfonation of dodecyltoluene, liquid n-butane is passed upwardly at a rate of 2500 grams per hour through a vertical pick-up zone containing 274 grams of liquid sulfur trioxide, a column of the reactor approximately 30 inches high. The pick-up zone is maintained at a temperature of about 18° C. and at 5 atmospheres pressure. At these conditions the n-butane carrying medium will contain approximately 3% by weight of sulfur trioxide. This mixture is then introduced into a sulfonation reactor containing 200 grams (0.77 mol) of dodecyl toluene. Sulfonation is effected at atmospheric pressure and at a temperature of about 0° C. obtained by cooling the n-butane. The vapors from the sulfonation reactor are condensed and a portion of the liquefied n-butane is returned to the reactor, while the remaining portion is utilized to pick up sulfur trioxide by recycling the butane to the pick-up zone. Under these conditions, approximately 97% sulfonation of the dodecyl toluene is obtained.

**Example II**

Utilizing the apparatus and procedure employed in Example I, the butane-sulfur trioxide effluent of the pick-up zone containing approximately 3% sulfur trioxide is introduced concurrently with lauryl alcohol into a stirred sulfonation reactor maintained at a temperature of approximately 0° C. at atmospheric pressure and at a rate sufficient to utilize about 1.1 moles of sulfur trioxide per mole of lauryl alcohol. The average residence time in the sulfonation reactor is about 15 minutes, the butane vaporizing as exothermic heat is liberated by the resulting sulfonation reaction. The butane vapors are continuously refluxed into the reactor by means of a Dry Ice condenser above the reactor. The resulting reaction mixture is continuously transferred to a distillation column for removal of the remaining butane and the distillation residue neutralized with caustic soda. Approximately 98% of the lauryl alcohol is sulfonated by this procedure and the product is substantially colorless.

**Example III**

Utilizing a vertical column pick-up zone, liquid butane is vaporized at atmospheric pressure and bubbled into the bottom of said pick-up zone containing liquid sulfur trioxide at a temperature of from about 20° to about 25° C. wherein it entrains sulfur trioxide vapor. The mixture of gases is then passed into a sulfonation reactor containing dodecyltoluene and about 1.5 volumes proportion of liquefied butane which refluxes into the reactor from a Dry Ice condenser attached to the sulfonation vessel. The butane-sulfur trioxide vapors are bubbled into the reactor as the liquid hydrocarbons are rapidly stirred, the heat of the resulting sulfonation reaction vaporizing the liquid butane which refluxes at a rate sufficient to maintain the volume proportion of butane to dodecyltoluene hydrocarbons in the sulfonation zone at approximately 1.5. Over 99% sulfonation is obtained and about 1% of sulfur trioxide are removed from the pick-up zone per mole of dodecyltoluene sulfonated.

We claim as our invention:

1. In a sulfonation process wherein a sulfonatable organic compound is reacted in a sulfonation zone with sulfur trioxide, the steps comprising heating sulfur trioxide to said zone which comprises maintaining in a pick-up zone apart from said sulfonation zone a mass of a sulfonating agent selected from the group consisting of liquid sulfur trioxide and solid sulfur trioxide, passing through said mass in the pick-up zone an inert paraffinic
hydrocarbon containing from 3 to 8 carbon atoms per molecule at a temperature below about 30°C. to entrain a portion of the sulfur trioxide in the paraffinic hydrocarbon, removing the resultant mixture of paraffinic hydrocarbon and sulfur trioxide from the pick-up zone and introducing the same to said sulfonation zone.

2. The method of claim 1 further characterized in that said paraffinic hydrocarbon is liquefied butane.

3. The process of claim 1 further characterized in that said inert paraffinic hydrocarbon is butane.

4. The process of claim 1 further characterized in that the γ-form of sulfur trioxide is maintained in said pick-up zone.

5. The process of claim 1 further characterized in that said inert paraffinic hydrocarbon is passed into said sulfur trioxide pick-up zone at a rate sufficient to supply said sulfonation zone with from about 1.1 to about 2 to 1 moles of sulfur trioxide per mole of sulfonatable organic compound.

6. The process of claim 1 further characterized in that the temperature and pressure conditions in said pick-up zone are selected to maintain said paraffinic hydrocarbon in substantially liquid phase therein.

7. The process of claim 1 further characterized in that said paraffinic hydrocarbon is introduced into said pick-up zone in the bottom thereof and in gaseous condition at a temperature sufficient to vaporize a portion of the sulfur trioxide in said pick-up zone to form a mixture of gases comprising said sulfur trioxide and said paraffinic hydrocarbon and thereafter passing said mixture into said sulfonation zone.

8. The process of claim 1 further characterized in that said paraffinic hydrocarbon is introduced into said pick-up zone in the bottom thereof and in gaseous condition at a temperature of from about 20°C to about 30°C to vaporize a portion of the sulfur trioxide in said pick-up zone to form a mixture of gases comprising said sulfur trioxide and said paraffinic hydrocarbon and thereafter passing said mixture into said sulfonation zone.

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