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PROCESS FOR THE SULFONATION OF ALKYL AROMATIC HYDROCARBONS

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This invention relates to an improved method for effecting sulfonation of alkyl aromatic hydrocarbons utilizable as intermediates in the formation of surface active agents and particularly detergents. More specifically, the invention consists of a method of sulfonation and of separating the sulfonation product whereby substantially complete conversion of the alkyl aromatic hydrocarbon charging stock is obtained and an improved product of high detergency is formed.

An object of this invention is to produce alkyl aryl sulfonates utilizable as detergents wherein substantially quantitative yields of product are obtained having desirable detergent properties and substantially free from undesirable colored materials and malodorous decomposition products.

A further object of this invention is to provide a process for sulfonating an alkyl aromatic hydrocarbon and converting the sulfonation product into the corresponding sulfonate salt utilizing a method in which a low ratio of sulfonating agent to alkyl aromatic hydrocarbon is employed and in which substantially quantitative conversion to sulfonation reaction product is obtained, thereby eliminating the necessity of neutralizing a large excess of sulfonating agent with a relatively costly neutralizing base.

Another object of this invention is to provide a process for sulfonating alkyl aromatic hydrocarbons for subsequent conversion into detergent compounds utilizing an oleum as sulfonating agent, in which process said oleum is reduced in viscosity at the low temperatures employed to effect the sulfonation reaction and is also enhanced in its sulfonating ability.

Still another object of this invention is to sulfonate an alkyl aromatic hydrocarbon so as to obtain nearly 100% conversion of the alkyl aromatic hydrocarbon charged into alkyl aryl sulfonate thereby eliminating the necessity of purifying the sulfonation product from non-sulfonated hydrocarbons which would normally be separated from the sulfonation product and recycled to the sulfonation reactor for further conversion or be permitted to remain in the detergent product and cause said product to have an odor of hydrocarbons undesirable for detergent use.

The present invention provides a process for sulfonating an alkyl aromatic hydrocarbon containing an alkyl group having from about 9 to about 18 carbon atoms wherein said alkyl aromatic hydrocarbon is contacted with an oleum sulfonating agent, said oleum sulfonating agent containing from at least 30 to about 65% by weight of sulfur trioxide in sulfuric acid. In the sulfonation treatment the amount of oleum used is such that from at least 0.8 to not more than 1.6 moles of free sulfur trioxide is present per mole of alkyl aromatic hydrocarbon. This sulfonation treatment is carried out in the presence of a substantially inert diluent capable of acting

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as a refrigerant by vaporizing during the sulfonation reaction. Suitable inert diluents consist of paraffinic and cycloparaffinic hydrocarbons having at least three but not more than eight carbon atoms per molecule and the halogenated unsulfonatable hydrocarbons of not more than 8 carbon atoms per molecule. When employing an inert diluent, a sulfonation reaction is carried out at a pressure sufficient to maintain at least a portion of said diluent in liquid phase during the sulfonation treatment and the inert diluent is then separated from the sulfonation reaction products and recycled to the process.

One specific embodiment of this invention comprises a process for sulfonating an alkyl aromatic hydrocarbon which comprises reacting said alkyl aromatic hydrocarbon with oleum containing from at least 30 to about 65% by weight of free sulfur trioxide in the presence of a substantially inert diluent maintained at least in part in the liquid phase for a time sufficient to sulfonate at least 95% by weight of said alkyl aromatic hydrocarbon, adding to the resultant sulfonation mixture an amount of water sufficient to convert the unused sulfur trioxide and sulfuric acid into a lower layer comprising essentially sulfuric acid monohydrate admixed with colored material, separating said lower layer from an upper layer comprising essentially alkyl aryl sulfonic acid and inert diluent, separating said diluent from said alkyl aryl sulfonic acids, and recovering said alkyl aryl sulfonic acids.

Another embodiment of this invention relates to a process for sulfonating an alkyl benzenoid hydrocarbon which comprises reacting said alkyl benzenoid hydrocarbon with oleum containing from at least 30 to about 65% by weight of free sulfur trioxide in the presence of a substantially inert diluent maintained at least in part in the liquid phase for a time sufficient to sulfonate at least 95% by weight of said alkyl benzenoid hydrocarbon, adding to the resultant sulfonation mixture an amount of water sufficient to convert the unused sulfur trioxide and sulfuric acid into a lower layer comprising essentially sulfuric acid monohydrate admixed with colored material, separating said lower layer from an upper layer comprising essentially alkyl aryl sulfonic acids and inert diluent, separating said diluent from said alkyl aryl sulfonic acids, and recovering said alkyl aryl sulfonic acids.

According to the process of this invention, a dodecyl toluene sodium sulfonate detergent is produced in the following manner: An alkyl toluene hydrocarbon fraction containing dodecyltoluene as a major component thereof, formed by the alkylation of toluene with a propylene tetramer fraction is contacted with oleum containing at least 30 to about 65% by weight of free sulfur trioxide, in a proportion of the oleum to the alkyl toluene corresponding to a mole ratio of free sulfur trioxide to hydrocarbon within the

range of from 0.9:1 to 1.3:1 at a temperature within the range of from about −20° to about +20° C., or preferably from about −10° to about +15° C., and in the presence of from about 1.6 to about 5 volumes of a C_4 paraffinic hydrocarbon fraction per volume of said alkyl aromatic hydrocarbon charge. About 0.5 to 3.5 volumes of this C_4 fraction per volume of the alkyl aromatic charge are maintained in the liquid phase in the sulfonation reaction mixture throughout the reaction, the pressure above the sulfonation reaction mixture being adjusted to a value sufficient to permit the remaining portion of said C_4 paraffinic hydrocarbon fraction to vaporize when the sulfonation temperature exceeds a pre-determined desired maximum, whereby excess heat is dissipated as heat of vaporization of the inert diluent and the reaction temperature is controlled and maintained at said desired maximum for the required period of sulfonation. To the resultant sulfonation mixture an amount of water is added which is sufficient to convert the unused sulfur trioxide and sulfuric acid into sulfuric acid monohydrate. The sulfuric acid monohydrate settles and forms as a lower layer a viscous, black, tarry phase comprising sulfuric acid monohydrate admixed with malodorous and colored materials. This lower layer is then separated from the upper layer which consists essentially of a butane solution of the dodecyltoluene sulfonic acid. The readily volatile portion of the butane solution is then vaporized and separated from the sulfonation reaction mixture either by reducing the pressure on the sulfonation reaction mixture or by increasing its temperature slightly or by both reducing the pressure and increasing the temperature. After removal of the butane from the upper layer of the sulfonation reaction product, the alkyl toluene sulfonic acid is neutralized by a dilute aqueous solution of sodium hydroxide, or of another alkali metal hydroxide, to form the alkali metal dodecyltoluene sulfonate detergent product.

The method may be applied with particular advantage to those alkyl aromatic hydrocarbons containing a monocyclic nucleus, that is the alkyl benzenoid derivatives, and it may also be utilized in the sulfonation of those alkyl aromatic hydrocarbons containing a polycyclic nucleus with similar and substantially advantageous results. The latter class of hydrocarbons which form a sulfonate utilizable as a detergent are typified, for example, by the alkylated naphthalenes, diphenyls, phenanthrenes, anthracenes, and the like compounds wherein the alkyl group contains from about 5 to about 10 carbon atoms per group such as amylmethylnaphthalene and nonylnaphthalene. Especially desirable detergents have been prepared from those alkyl benzenoid hydrocarbons containing at least two nuclear alkyl groups, not more than one of which is an alkyl group containing from about 9 to about 18 carbon atoms per group and the remaining alkyl groups of which contain not more than two carbon atoms per group, preferably not more than one carbon atom per group. It is also preferred in the production of alkyl benzenoid sulfonates that the alkyl benzenoid hydrocarbon charged to the sulfonation reaction contain not more than two short chain alkyl substituents, and the latter, if they are present, are preferably methyl radicals.

In the production of the alkyl aromatic hydrocarbon charging stocks of the benzenoid type, an aromatic hydrocarbon such as benzene, toluene, xylene, methylethyl benzene, or diethyl benzene is condensed or alkylated with an alkylating agent capable of providing an alkane hydrocarbon radical having from about 9 to about 18 carbon atoms per group. In a typical preparation of the alkyl aromatic hydrocarbon, toluene may be alkylated with a mono-olefinic hydrocarbon fraction in which the components contain from 9 to about 18 carbon atoms per molecule in the presence of a suitable catalytic agent selected from those catalysts known generally to the art as alkylation catalysts, such as concentrated sulfuric acid, substantially anhydrous hydrogen fluoride, an aluminum halide and the like. Desirable olefinic hydrocarbon fractions containing components of relatively straight or but slightly branched chain olefins produced, for example, by the polymerization of lower molecular weight olefins such as propylene and/or butylene or derived from suitably boiling fractions recovered from cracked petroleum products such as a pressure distillate fraction of a thermal cracking operation boiling from about 140° to about 300° C., but preferably from about 170° to about 240° C., may be employed as alkylating agents to form the alkyl aromatic hydrocarbon charging stock to be sulfonated. Another method of preparing alkyl aromatic hydrocarbons suitable for detergent production is by the condensation of a halogenated alkane, for example, a chlorinated kerosene derived from a hydrocarbon distillate boiling from about 170° to about 240° C., with a desirable aromatic hydrocarbon in the presence of a condensation reagent such as anhydrous aluminum chloride. The desirable alkyl aromatic hydrocarbon is separated from the alkylation and/or condensation reaction products by distillation and a fraction corresponding to an alkylate containing an alkyl group having from about 9 to about 18 carbon atoms per group is separated as a specific fraction therefrom, which in the case of benzene or toluene boils at a temperature of from about 275° to about 345° C.

In the investigation of suitable sulfonation techniques it has been observed that the alkyl aromatic hydrocarbon charge, as prepared by the processes outlined above, may be sulfonated without appreciable dealkylation of the charging stock by utilizing an oleum in which free sulfur trioxide is present (that is, sulfur trioxide present in quantities greater than that combined with water in sulfuric acid, H_2SO_4), the sulfonation reaction generally being effected at temperatures below about 20° C. It was further observed, however, that when utilizing oleums in which the sulfur trioxide content was below about 30%, a large excess of acid beyond that necessary for monosulfonation of the alkylate was required in order to obtain reasonably complete sulfonation in a single contact period between the oleum and the alkyl aromatic hydrocarbon.

In the manufacture of detergents of the dodecyltoluene sodium sulfonate type, superior sulfonation results are obtained by carrying out this reaction with highly concentrated oleum, that is, oleum containing at least 30% by weight of free sulfur trioxide, at a relatively low temperature, generally of from about −10° to about +20° C., in the presence of at least 1.5 volumes of internal coolant-diluent such as butane per volume of dodecyltoluene. This combination of conditions results in economy of sulfuric acid-sulfur trioxide sulfonating agents since only slightly more than one mole of free sulfur trioxide is used per mole of dodecyltoluene sulfonated. Although the sul-

fonation reaction is almost quantitative, a relatively small amount of sulfonating agent remains in the sulfonation reaction mixture with a resulant saving in the amount of caustic required for neutralization of this excess of sulfuric acid sulfonating reagent. Such a procedure yields a final neutralized detergent composition containing approximately 70% by weight of dodecyltoluene sodium sulfonate and 30% by weight of sodium sulfate.

We have now found that a detergent of greatly improved quality (higher detergent value, less odor, and light color) and containing over 90% by weight of dodecyltoluene sodium sulfonate can be prepared by an improvement in the procedure which comprises the addition of water to the sulfonation mixture at the conclusion of the sulfonation treatment in an amount such that the unconverted sulfur trioxide and the unused sulfuric acid are converted to the approximate composition of the monohydrate, $H_2SO_4 \cdot H_2O$. We have found, as a result of numerous experiments, that the amount of water required for sufficient dilution of the reaction mixture may be expressed approximately by the equations:

(1) $$W = n[2(S - 0.95) + S^1]$$

when $S \geq 1$ and

(2) $$W = n(S^1 + 0.1)$$

when $S < 1$, where W=number of mols of water to be added, S=number of mols of free sulfur trioxide per mol of alkylate charged to the sulfonation, S^1=number of mols of 100% sulfuric acid per mol of alkylate charged to the sulfonation, and n=number of mols of alkylate charged to the sulfonation. This amount of water is sufficient to make sulfuric acid monohydrate, i. e. sulfuric acid of about 84.5% strength (neglecting the other components present) or more broadly speaking, acid of about 80 to about 85% strength which we have found effects the purpose of our invention.

This addition of water is effected in the presence of the butane solvent or other low boiling inert diluent that is used, and the reaction mixture containing the added water is permitted to settle whereby a viscous, black, tarry phase comprising principally sulfuric acid monohydrate admixed with colored and malodorous material settles out as a lower layer. The lower layer containing the sulfuric acid monohydrate is then separated from the upper layer comprising essentially a butane solution of dodecyltoluene sulfonic acid. The solution of dodecyltoluene sulfonic acid in butane which is a fluorescent greenish liquid with low viscosity is then subjected to suitable separation treatment to remove butane. This separation of butane is effected by lowering the pressure or by slightly increasing the temperature or by use of both methods simultaneously in order to obtain dodecyltoluene sulfonic acid containing not more than about 10% of butane, and thereafter the dodecyltoluene sulfonic acid is neutralized with a water soluble base preferably sodium hydroxide to form the alkali metal salt of dodecyltoluene sulfonic acid, said metal salt particularly the sodium salt being useful as a detergent.

When this procedure of separating unused sulfur trioxide and sulfuric acid as essentially sulfuric acid monohydrate is employed in conjunction with a sulfonation product wherein oleum of more than 30% free sulfur trioxide content is employed as a sulfonating reagent at a temperature of about 0° C. and sufficient oleum is utilized to effect about 95% sulfonation, the neutralized sulfonic acids recovered as a product of our improved method have a purity of about 95%, that is, the detergent contains about 95% by weight of dodecyltoluene sodium sulfonate and about 5% of sodium sulfate. Such a mixture of dodecyltoluene sodium sulfonate and sodium sulfate has a high detergent power, is white in color, and substantially odorless. The colored and malodorous materials which sometimes form during the sulfonation treatment are removed almost completely in the tarry material that is admixed with the sulfuric acid monohydrate phase.

In contrast to these results, the normal method of separating unused sulfuric acid and sulfur trioxide from alkyl aryl sulfonic acids in a sulfonation mixture resulting from the use of lower strength oleum, yields a sulfonic acid product which on neutralization, gives a sodium sulfate-sodium alkyl aryl sulfonate mixture containing at least about 25% by weight of sodium sulfate, and usually less than about 75% by weight of sodium alkyl aryl sulfonate, as well as small amounts of colored materials and malodorous components.

In the present process free sulfur trioxide in any of its various physical modifications may be used by itself as the sulfonating agent. Thus the alpha- and beta-forms of sulfur trioxide which are normally solids at the operating temperatures herein specified and alpha-sulfur trioxide, the normally liquid form of the reagent, are each utilizable for sulfonating alkyl aromatic hydrocarbons in the presence of the inert diluent to effect nearly quantitative conversion of the charge at molar ratios of sulfur trioxide to alkylate as low as about 1.1 to 1. While greater ratios of sulfur trioxide to alkylate may be employed in this embodiment according to the present invention, quantities of sulfur trioxide in the sulfonation reaction mixture substantially in excess of the above 1.1 to 1 molar ratio, are not quantitatively utilized and tend toward polysulfonation, which is generally considered undesirable, especially in the sulfonation of alkyl aromatic hydrocarbons to form detergent intermediates.

The advantageous results obtained when utilizing a sulfonating agent containing at least 30% free sulfur trioxide such as a highly concentrated oleum in the presence of the inert diluent at selective sulfonating conditions are believed to be due, at least partly, to the dispersing effect of the diluent on the oleum when contacting the alkylate to be sulfonated. When the oleum is charged into a sulfonation reactor containing the alkylate in the absence of a diluent, the direct contact of the oleum with the alkylate appears to result in local high temperatures which have the tendency of effecting the cleavage of the long chain alkyl groups from the alkylate and also of effecting oxidation and at least partial polymerization of the olefinic fragments resulting from the cleavage. The effect of the polymerization is to form resinous and tarry products possessing an undesirable color as well as forming water-insoluble organic materials which become entrained with the final detergent product and which impart a sticky feeling to the detergent as well as to objects washed in its aqueous solutions. Furthermore, the sulfonic acids produced by de-alkylated alkyl aromatic charging stock are of inferior detergency and since they become mixed with the final product, the latter possesses a lower total detergency. In the presence of the diluent, on

the other hand, the oleum and alkylate are dispersed such that the reaction proceeds more smoothly and relatively smaller portions of the alkylate are contacted by the sulfonating agent immediately upon the introduction of the latter into the alkylate-diluent mixture. Furthermore, since the diluent is desirably a low boiling inert compound, the rise in temperature resulting from sulfonation vaporizes a portion of the diluent and the resulting cooling or self-refrigeration effect removes the heat of sulfonation reaction and maintains the reaction temperature at a substantially constant level, thereby eliminating the local high temperatures encountered in the absence of the diluent.

The neutralized product of the sulfonic acids formed in the sulfonation reaction is ordinarily admixed prior to utilization with certain inorganic salts which tend to enhance the activity of the detergent. One of the preferred classes of salts utilizable for this purpose, referred to in the art as "builder" salts, are the alkali metal sulfates, such as those formed by neutralizing sulfuric acid with an alkali metal hydroxide. Other "builders" are the alkali metal phosphates and polyphosphates, silicates, carbonates, borates, borates, and the like. In the preparation of the final detergent composition containing the builder salt plus the alkyl aromatic sulfonate, one procedure which may be followed is to neutralize the sulfonic acid-sulfonating agent reaction mixture recovered from the sulfonation stage and thereby convert the excess sulfonating agent to the sulfate salt of the neutralizing agent. In practice, however, it is desirable to form as little of the sulfate salts as possible by neutralization, since purchased sulfate salts are cheaper than those made by neutralizing the sulfuric acid with a neutralizing agent and since other builders such as those listed above may be desired instead of or in addition to the sulfate.

When a higher ratio of builder salt to alkyl aromatic sulfonate is desired in the final detergent composition additional builder salts may be added from an extraneous source to the neutralization mixture. This procedure permits production in an economical manner of detergent compositions in which the preferred proportion by weight of builder salt to sulfonate is within the range of from about 1:1 to about 5:1 of builder salt of the sulfonate.

The diluent herein specified for utilization in the sulfonation reaction mixture is more specifically characterized as a normally liquid or liquefiable substance which is essentially inert at the sulfonating conditions employed to effect sulfonation of the alkylate and which is capable of being vaporized from the sulfonation reaction mixture at temperatures in the proximity of the sulfonation reaction temperature. The diluent thus may be a material which boils normally at a temperature approximately equal to or below the desired sulfonation reaction temperature, or it may be a material which can be induced by suitable pressure regulation to boil at a temperature about equal to or below the desired sulfonation reaction temperature so that in any event it can also be retained in the liquid phase in the sulfonation reaction mixture by regulation of the pressure thereon. The preferred diluents are the inert paraffinic hydrocarbons containing at least three carbon atoms per molecule and not more than about 8 carbon atoms per molecule such as liquefied propane, butane, pentane and isomers, homologs, or mixtures thereof which

boil at such temperatures and pressures that said hydrocarbons may be utilized in the capacity of an internal refrigerant when they evaporate at the desired sulfonation temperature. Non-reactive cycloparaffins i. e. those of the cyclopentane or cyclohexane series boiling in the same range may also be used. Another class of compounds utilizable as diluents include the mono- or polyhalogenated hydrocarbons containing not more than eight carbon atoms per molecule such as the fluorinated, chlorinated, and/or brominated hydrocarbons represented, for example, by such compounds as trichloroethane, hexachlorocyclohexane, "freon" (dichlorodifluoromethane) or a halogenated hydrocarbon wherein all of the halogen atoms of the hydrocarbon analog are replaced by halogen atoms such as the halocarbons, represented for example by carbon tetracholride, carbon tetrafluoride, perfluoropropane, and perfluorobutane.

An especially desirable inert diluent is normal butane or a mixture of the various butanes or a mixture of butanes and propane which boils at temperatures of from about −15° to about 0° C., at atmospheric pressure. Another preferred diluent is represented by the fluorocarbons containing up to about 5 carbon atoms per molecule such as perfluoropropane and perfluorobutane.

In the sulfonation of dodecyltoluene, the sulfonation temperature is desirably maintained at from about −20° to about +20° C. preferably at a temperature of from −10° to +15° C. and as hereinbefore indicated, the pressure above the sulfonation reaction mixture is maintained at a value sufficient to keep in the liquid phase at least a portion of the inert diluent present within the reaction mixture, although said pressures are also desirably maintained at such value that the diluent will evaporate and provide evaporation cooling when the sulfonation reaction mixture tends to exceed the desired temperature. In the case of butane, for example, the sulfonation reaction may be operated at substantially atmospheric pressure when the sulfonation temperature is maintained at about 0° C.

Reaction periods of from about 5 to about 45 minutes are generally sufficient to effect substantially complete sulfonation of the alkyl aromatic charge, the preferred time of reaction being about 15 to about 20 minutes. The volume ratio of liquid diluent to alkylate charging stock maintained in the sulfonation reactor during the sulfonation reaction depends somewhat on the particular diluent used and is maintained within the range of from about 0.7:1 to about 5:1, in the case of sulfur dioxide and from about 1.6:1 to about 5:1 in the case of butane as diluent, where said volume ratio is calculated on the basis of both the components being in the liquid state. It is generally preferred to maintain said volume ratio at more than 1.5 or 2 liquid volumes of diluent to alkylate so as to assure not only that sufficient diluent is available for vaporization during the reaction to effect the desired self-refrigerating advantages hereinabove noted, but also that sufficient diluent is retained in liquid phase to provide for the diluting effects also noted above. The ratios vary for each diluent specified, depending upon the heat of vaporization for each. Furthermore, at the above preferred ratio, the quantity of diluent to be evaporated from the sulfonation reaction mixture following completion of the sulfonation reaction is not excessive, does not require large quantities of heat to effect the evaporation of the diluent from the sulfonation

reaction mixture, and does not demand excessive compressor duty to reliquefy the vaporized diluent.

The present process may be operated in either a batch or continuous type of operation, although continuous operation is generally preferred since all of the various factors present in the operation may be maintained at substantially equilibrium during the process. In a typical continuous method of operation, the diluent herein specified may be added to the alkylate in the desired proportion, the resultant mixture then being cooled or heated to the desired sulfonation reaction temperature and subsequently contacted with the oleum to effect sulfonation, the various charging stocks being mixed in a flowing stream of the same. During the course of the reaction, the mixture may be agitated with the aid of a suitable stirring device such as a revolving paddle or baffle mixers in order to obtain desirable intimate contact between the reactants and diluent charged to the process. Following the desired period of contact, the reaction mixture is admixed with sufficient water to convert the excess sulfur trioxide and used sulfuric acid into sulfuric acid monohydrate and the resultant mixture is then transferred to a settling tank or other suitable vessel in which the mixture may stand during a time sufficient for the sulfuric acid monohydrate to separate as a lower layer from the upper layer comprising essentially a solution of the alkyl aryl sulfonic acid dissolved in the inert diluent such as butane. After the sulfuric acid monohydrate has been separated from the upper layer, the latter is subjected to flashing or distillation treatment to remove the inert diluent from the alkyl aryl sulfonic acid and the latter is then charged directly to a neutralization tank or it may be diluted with water and then reacted with an aqueous solution of sodium hydroxide or another water soluble base to form the alkali metal salt of the alkyl aryl sulfonic acid. Such an aqueous solution of an alkali metal salt of an alkyl aryl sulfonic acid may be dried by suitable means such as spray drying to produce the detergent in solid form such as granules.

The process of this invention is illustrated further by the following example although the data presented therein should not be misconstrued to limit unduly the broad scope of the invention.

An alkyl aromatic sulfonate detergent composition containing a detergent component, a major proportion of which is sodium dodecyltoluene sulfonate, and also containing sodium sulfate as a builder salt, was prepared by a series of reaction steps comprising the continuous alkylation of toluene with a propylene tetramer fraction, sulfonation of a selected fraction of said toluene alkylate with 65% oleum in accordance with the method herein provided, neutralization of the resulting sulfonation reaction mixture, blending of the aqueous solution formed thereby with sodium sulfate to increase the concentration of the latter component to its optimum proportion therein, and drying the resultant aqueous composition of detergent salt and builder salt. The series of successive reaction steps is described as follows:

Alkylation treatment

A technical grade toluene of 97% purity was continuously commingled with a propylene tetramer fraction boiling from about 170° to about 225° C. produced by the polymerization of a propane-propylene fraction over a "solid phosphoric acid catalyst" (that is, a catalyst formed by calcining a mixture of kieselguhr and pyrophosphoric acid), with the flow rates of the respective hydrocarbon streams being adjusted to provide an aromatic:olefin mole ratio of about 7. The resulting mixture was charged into an alkylation autoclave at an average rate of 488.7 ml./hr. wherein it was contacted with sulfuric acid to effect alkylation of the toluene with the olefins contained in the propylene tetramer fraction. Fresh sulfuric acid having a concentration of 98.5% H_2SO_4 charged into the alkylation autoclave at a rate of 44.4 ml./hr. was mixed with recycle acid charged at a rate of 121.2 ml./hr. and the resulting mixture of acids contacted with the hydrocarbon charge at atmospheric pressure and at a temperature of 2.5° C. with stirring, for a total space-time of 30 minutes. The effluent stream of reaction products from the alkylation reactor was allowed to stand quiescent to allow the hydrocarbon therein to separate from the used alkylation acid. The upper hydrocarbon layer was decanted from the mixture, washed with water and fractionated. A fraction boiling from about 275° to about 345° C., representing the toluene alkylate fraction to be utilized for detergent production, and the excess toluene were separated as individual fractions and the latter toluene fraction was recycled to the alkylation reactor. The alkylate product was formed at the rate of 1.332 kilograms per kilogram of olefin charged.

Sulfonation treatment

One volume of the toluene alkylate prepared as described above was dissolved in 1.6 volumes of n-butane, the temperature being maintained at about 0° C. by permitting the butane to reflux into a Dry Ice condenser. The mixture was stirred rapidly as 1.8 moles of 65% oleum per mole of alkylate, corresponding to 1.25 moles of free sulfur trioxide per mole of alkylate, was introduced gradually into the mixture. As the oleum was added, the n-butane refluxed and maintained the temperature of the mixture practically constant at about 0° C. The oleum was added during a period of about 15 minutes per mole of alkylate and following the addition of oleum, the resulting mixture was stirred for an additional time of 30 minutes. A determination of the amount of unsulfonated alkylate in the sulfonation reaction mixture by extraction of the mixture with pentane and evaporation of the pentane extractant indicated that 96% of the alkylate underwent sulfonation. To the sulfonation reaction mixture comprising dodecyltoluene sulfonic acid, butane diluent, excess sulfur trioxide, and sulfuric acid was added 1.15 mols of water per mol of alkylate originally charged, which was calculated as sufficient to convert the unused sulfur trioxide and sulfuric acid into sulfuric acid monohydrate. The water treated reaction mixture was then permitted to stand for one-half hour, during which a black, tarry, rather viscous lower layer separated from the substantially non-viscous fluorescent greenish upper layer containing dodecyltoluene sulfonic acid dissolved in the butane diluent. The lower layer containing sulfuric acid monohydrate and tar was then withdrawn and discarded and the butane solution of the dodecyltoluene sulfonic acid was introduced into a fractionating column maintained at a temperature of about +10° C. and the butane was distilled overhead and condensed to a liquid for further recycling to the process. The residue after vaporization of the butane diluent therefrom was diluted with 0.5

volume of water per volume of dodecyltoluene sulfonic acid and the resulting solution was mixed with an aqueous solution containing 20% by weight of sodium hydroxide until a pH of approximately 7 was obtained. The ratio of sodium sulfate to sodium dodecyltoluene sulfonates in the aqueous solution of neutral salts was approximately one part by weight of sodium sulfate to 19 parts by weight of sodium dodecyltoluene sulfonates.

Drying treatment

The aqueous solution of the mixture of sodium sulfate and sodium dodecyltoluene sulfonates resulting from the aforementioned neutralization treatment was charged to a spray drying apparatus at a temperature of approximately 100° C. to evaporate the water therefrom and form substantially spherical particles of detergent composition. Air at a temperature of about 300° C. was introduced into the spray drying chamber countercurrent to the sprayed solution of detergent composition salts, resulting in the formation of dry, spherically shaped particles of said composition having sizes in the range of from about 100 mesh to about 180 mesh (from about 0.15 to about 0.08 mm. diameters). The resulting composition when dissolved in water at 60° C. had a detergency superior to that of sodium stearate when tested under similar conditions.

We claim as our invention:

1. A process for sulfonating an alkyl aromatic hydrocarbon which comprises reacting said alkyl aromatic hydrocarbon with oleum containing from at least 30 to about 65% by weight of free sulfur trioxide in the presence of a substantially inert diluent consisting essentially of at least one saturated hydrocarbon containing from 3 to 8 carbon atoms per molecule maintained at least in part in the liquid phase for a time sufficient to sulfonate at least 95% by weight of said alkyl aromatic hydrocarbon, adding to the resultant sulfonation mixture only such an amount of water as to convert the unused sulfur trioxide and sulfuric acid into a lower layer comprising essentially sulfuric acid monohydrate, separating said lower layer from an upper layer comprising essentially alkyl aryl sulfonic acids and inert diluent, separating said diluent from said alkyl aryl sulfonic acids and recovering said alkyl aryl sulfonic acids.

2. A process for sulfonating an alkyl benzenoid hydrocarbon which comprises reacting said alkyl benzenoid hydrocarbon with oleum containing from at least 30 to about 65% by weight of free sulfur trioxide in the presence of a substantially inert diluent consisting essentially of at least one saturated hydrocarbon containing from 3 to 8 carbon atoms per molecule maintained at least in part in the liquid phase for a time sufficient to sulfonate at least 95% by weight of said alkyl benzenoid hydrocarbon, adding to the resultant sulfonation mixture only such an amount of water as to convert the unused sulfur trioxide and sulfuric acid into a lower layer comprising essentially sulfuric acid monohydrate, separating said lower layer from an upper layer, comprising essentially alkyl aryl sulfonic acids and inert diluent, separating said diluent from said alkyl aryl sulfonic acids, and recovering said alkyl aryl sulfonic acids.

3. A process for sulfonating an alkyl toluene in which said alkyl group contains from 9 to 18 carbon atoms with oleum containing from at least 30 to about 65% by weight of free sulfur trioxide in the presence of a diluent consisting essentially of at least one saturated hydrocarbon containing from 3 to 8 carbon atoms per molecule maintained at least in part in the liquid phase for a time sufficient to sulfonate at least 95% by weight of said alkyl toluene, adding to the resultant sulfonation mixture only such an amount of water as to convert the unused sulfur trioxide and sulfuric acid into a lower layer comprising essentially sulfuric acid monohydrate, separating said lower layer from an upper layer comprising essentially alkyl toluene sulfonic acid and hydrocaron diluent, and recovering said alkyl toluene sulfonic acid.

4. A process for sulfonating dodecyltoluene with oleum containing from at least 30 to about 65% by weight of free sulfur trioxide in the presence of a diluent consisting essentially of butane maintained at least in part in the liquid phase for a time sufficient to sulfonate at least 95% by weight of said dodecyltoluene, adding to the resultant sulfonation mixture only such an amount of water as to convert the unused sulfur trioxide and sulfuric acid into a lower layer comprising essentially sulfuric acid monohydrate, separating said lower layer from an upper layer comprising essentially dodecyltoluene sulfonic acid and butane, and recovering said dodecyltoluene sulfonic acid.

5. A process for producing a detergent which comprises sulfonating dodecyltoluene with oleum containing from at least 30 to about 65% by weight of free sulfur trioxide at a temperature of from about −20° to about +20° C. in the presence of a diluent consisting essentially of butane maintained at least in part in the liquid phase for a time sufficient to sulfonate at least 95% by weight of said dodecyltoluene, adding to the resultant sulfonation mixture only such an amount of water as to convert the unused sulfur trioxide and sulfuric acid into a lower layer comprising essentially sulfuric acid monohydrate, separating said lower layer from an upper layer comprising essentially dodecyltoluene sulfonic acid and butane, neutralizing said dodecyltoluene sulfonic acid with an aqueous solution of an alkali metal hydroxide, and recovering the alkali metal salt of said dodecyltoluene sulfonic acid.

6. In a process for sulfonating dodecyltoluene by reacting said hydrocarbon with oleum containing from at least 30 to about 65% by weight of free sulfur trioxide at a temperature of from about −20° to about +20° C. in the presence of a diluent consisting essentially of butane maintained at least in part in the liquid phase for a time sufficient to sulfonate about 95% by weight of said dodecyltoluene, the improvement which comprises adding to the resultant sulfonation mixture only such an amount of water as to convert the unused sulfur trioxide and sulfuric acid into a lower layer comprising essentially sulfuric acid monohydrate, separating said lower layer from an upper layer comprising essentially dodecyltoluene sulfonic acid and butane diluent, separating said butane diluent from said dodecyltoluene sulfonic acid, and recovering said dodecyltoluene sulfonic acid.

7. In a process for producing a detergent which comprises sulfonating an alkyl aromatic hydrocarbon by reacting said alkyl aromatic hydrocarbon with oleum containing from at least 30 to about 65% by weight of free sulfur trioxide at a temperature of from about −20° to about +20° C. in the presence of a diluent consisting essentially of at least one paraffinic hydrocarbon containing from 3 to 8 carbon atoms per molecule

maintained at least in part in the liquid phase for a time sufficient to sulfonate about 95% by weight of said alkyl aromatic hydrocarbon, the improvement which comprises adding to the resultant sulfonation mixture only such an amount of water as to convert the unused sulfur trioxide and sulfuric acid into a lower layer comprising essentially sulfuric acid monohydrate, separating said lower layer from an upper layer comprising essentially alkyl aryl sulfonic acid and paraffinic hydrocarbon diluent, separating said paraffinic hydrocarbon diluent from said alkyl aryl sulfonic acid, neutralizing said alkyl aryl sulfonic acid with an aqueous alkali metal hydroxide to form an aqueous solution of an alkali metal alkyl aryl sulfonate, and recovering said alkali metal alkyl aryl sulfonate from said solution.

8. A process for sulfonating an alkyl aromatic hydrocarbon which comprises reacting said alkyl aromatic hydrocarbon with oleum containing at least 30% by weight of free sulfur trioxide in the presence of a substantially inert diluent consisting essentially of at least one saturated hydrocarbon containing from 3 to 8 carbon atoms per molecule maintained at least in part in the liquid phase for a time sufficient to sulfonate at least 95% by weight of said alkyl aromatic hydrocarbon, adding to the resultant sulfonation mixture only such an amount of water as to convert the unused sulfur trioxide and sulfuric acid into a lower layer comprising essentially sulfuric acid monohydrate, separating asid lower layer from an upper layer comprising essentially alkyl aryl sulfonic acid and inert diluent, separating said diluent from said alkyl aryl sulfonic acid and recovering said alkyl aryl sulfonic acids.

9. A process for sulfonating an alkyl toluene in which said alkyl group contains from 9 to 18 carbon atoms with oleum containing at least 30% by weight of free sulfur trioxide in the presence of a diluent consisting essentially of at least one saturated hydrocarbon containing from 3 to 8 carbon atoms per molecule maintained at least in part in the liquid phase for a time sufficient to sulfonate at least 95% by weight of said alkyl toluene, adding to the resultant sulfonation mixture only such an amount of water as to convert the unused sulfur trioxide and sulfuric acid into a lower layer comprising essentially sulfuric acid monohydrate, separating said lower layer from an upper layer comprising essentially alkyl toluene sulfonic acid and hydrocarbon diluent, and recovering said alkyl toluene sulfonic acid.

10. A process for sulfonating an alkyl aromatic hydrocarbon which comprises reacting said alkyl aromatic hydrocarbon with oleum containing from at least 30 to about 65% by weight of free sulfur trioxide in the presence of a substantially inert diluent consisting essentially of at least one saturated hydrocarbon containing from 3 to 8 carbon atoms per molecule maintained at least in part in the liquid phase for a time sufficient to sulfonate at least 95% by weight of said alkyl aromatic hydrocarbon, adding to the resultant sulfonation mixture only such an amount of water as to convert the unused sulfur trioxide and sulfuric acid into a lower layer comprising essentially aqueous sulfuric acid of from about 80 to about 85% H_2SO_4 content, separating said lower layer from an upper layer comprising essentially alkyl aryl sulfonic acids and inert diluent, separating said diluent from said alkyl aryl sulfonic acids and recovering said alkyl aryl sulfonic acids.

11. A process for sulfonating an alkyl toluene in which said alkyl group contains from 9 to 18 carbon atoms with oleum containing from at least 30 to about 65% by weight of free sulfur trioxide in the presence of a diluent consisting essentially of at least one saturated hydrocarbon containing from 3 to 8 carbon atoms per molecule maintained at least in part in the liquid phase for a time sufficient to sulfonate at least 95% by weight of said alkyl toluene, adding to the resultant sulfonation mixture only such an amount of water as to convert the unused sulfur trioxide, and sulfuric acid into a lower layer comprising essentially aqueous sulfuric acid of from about 80 to about 85% H_2SO_4 content, separating said lower layer from an upper layer comprising essentially alkyl toluene sulfonic acid and hydrocarbon diluent, and recovering said alkyl toluene sulfonic acid.

12. In a process for sulfonating dodecyltoluene by reacting said hydrocarbon with oleum containing from at least 30 to about 65% by weight of free sulfur trioxide at a temperature of from about −20° to about +20° C. in the presence of a diluent consisting essentially of butane maintained at least in part in the liquid phase for a time sufficient to sulfonate about 95% by weight of said dodecyltoluene, the improvement which comprises adding to the resultant sulfonation mixture only such an amount of water as to convert the unused sulfur trioxide and sulfuric acid into a lower layer comprising essentially aqueous sulfuric acid of from about 80 to about 85% H_2SO_4 content, separating said lower layer from an upper layer comprising essentially dodecyltoluene sulfonic acid and butane diluent, separating said butane diluent from said dodecyltoluene sulfonic acid, and recovering said dodecyltoluene sulfonic acid.

13. A process for sulfonating an alkyl aromatic hydrocarbon which comprises reacting said alkyl aromatic hydrocarbon with oleum containing at least 30% by weight of free sulfur trioxide in the presence of a substantially inert diluent consisting essentially of at least one saturated hydrocarbon containing from 3 to 8 carbon atoms per molecule maintained at least in part in the liquid phase for a time sufficient to sulfonate at least 95% by weight of said alkyl aromatic hydrocarbon, adding to the resultant sulfonation mixture only such an amount of water as to convert the unused sulfur trioxide and sulfuric acid into a lower layer comprising essentially sulfuric acid monohydrate, separating said lower layer from an upper layer comprising essentially alkyl aryl sulfonic acid and inert diluent, neutralizing said alkyl aryl sulfonic acid, and recovering the resultant salt of said alkyl aryl sulfonic acid.

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