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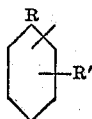
SULFONATION OF POLY-ALKYL SUBSTITUTED AROMATIC HYDROCARBONS

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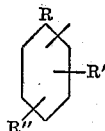
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7 Claims. (Cl. 260—505)

This invention relates to the sulfonation of hydrocarbons and more particularly to a process of sulfonating polysubstituted aromatic hydrocarbons in the production of alkyl aromatic sulfonic acids or salts thereof having surface-active properties. The invention is especially useful in the sulfonation of polyalkyl-substituted aromatic hydrocarbon mixtures which are conveniently referred to hereinafter as alkylated homologues of benzene. Such compounds may be represented by the following general formulae



and



wherein R represents a straight or branched aliphatic chain containing from about 10 to 18 carbon atoms, R' and R'' are short-chain alkyl radicals of from 1 to 3 carbon atoms. Hydrocarbons of this class, or mixtures thereof, have been prepared heretofore, for example by suitably condensing an olefin hydrocarbon fraction boiling between about 150° and 275° C. with toluene or xylene, or the like homologue of benzene, to provide a hydrocarbon mixture or alkane distilling within a range of about 250° to 400° C., the boiling temperature ranges being at ordinary atmospheric pressure conditions, i. e. 760 mm. of mercury.

One method of preparing such alkylated aromatic compounds comprises the chlorination of a kerosene, or similar close-cut petroleum fraction e. g. boiling between 150° and 275° C., as described, and catalytically condensing the resultant chlorinated compound with an aromatic hydrocarbon. The alkyl aromatic compound thus formed is then suitably sulfonated to produce a monosulfonated alkylated aromatic product, the sulfo group being attached to the aromatic ring. The water-soluble sulfonates, as well as the alkali, alkali-metal or ammonium salts, of these alkylated aryl hydrocarbons or alkanes have distinctive surface-active properties which make them suitable for use as detergents and wetting and emulsifying agents.

Such alkyl aryl hydrocarbon mixtures heretofore, however, have been difficult to sulfonate to produce a product which is of good color and free from objectionable odors, and having a high yield of alkyl aryl sulfonate. Moreover, generally a large excess of the sulfonating agent has been required to effect sulfonation. Another difficulty encountered has been that de-alkylation of the hydrocarbon takes place to an undesirable extent with the formation of lower sulfonated side-reaction products and unsulfonated residues. The presence of such lower sulfonated reaction products and unsulfonated residues in the sulfonated product is highly undesirable because the detergency power is decreased thereby. Further, such by-products tend to impart color and/or odor to the sulfonated mixture and give it a tackiness which

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lessens the commercial value of the product particularly for detergent purposes. The use of large excesses of the sulfonating agent also is undesirable especially where the resultant sulfonate mixture is to be neutralized to provide a water-soluble salt having a high proportion of alkyl aryl sulfonate salt.

The present invention provides an improved process of carrying out the sulfonation of such alkyl substituted aromatic hydrocarbon mixtures to obtain a yield of upwards of 90% while employing a minimum quantity of the sulfonating agent. The method permits the sulfonation reaction to be carried out at fairly low temperatures and which are commercially practicable. Decomposition of the alkylated hydrocarbons during sulfonation and the formation of detrimental side-reaction products are largely prevented whereby a sulfonated mixture is produced which is light in color and relatively free from objectionable odors and stickiness which heretofore have characterized such sulfonated mixtures. Further, employing the method of the invention there is produced a sulfonic acid product which after neutralization gives a composition containing about 50% by weight of sulfonated alkyl aryl material, which is the active ingredient. By so doing, the inclusion of builders or the like substances, for enhancing the detergency properties such as soil-removing power, foaming and/or wetting characteristics of the detergent is permitted without lowering the percentage content of the organic sulfonate salt to such an extent that the efficiency of the product is detrimentally affected.

In accordance with the invention the sulfonation of these alkylated homologues of benzene may be accomplished with the production of a high yield of alkyl aryl sulfonic acid, for example between 95 and 100%, by carrying out the sulfonation in the presence of a relatively large amount of phosphorus pentoxide or suitable compound containing phosphorus pentoxide. Compounds which have been found particularly effective for this purpose, when used in substantial amounts, for example such as to provide at least about 5% by weight of P₂O₅ based on the weight of alkylated aryl hydrocarbon mixture being sulfonated, are phosphorus pentoxide and phosphoric acid derivatives thereof, especially tetraphosphoric acid. Phosphorus pentoxide and the phosphoric acid derivatives are referred to in the annexed claims as "phosphorus pentoxide catalyst" and it will be understood that such terminology connotes both phosphorus oxide derivatives as well as phosphorus pentoxide.

The reason for the high sulfonation yield and improved quality of the product obtained by carrying out the sulfonation in the presence of a comparatively large amount of phosphorus pentoxide or oxygen-containing phosphorus compound providing an equivalent amount of P₂O₅, is not understood and appears to bear no particular relationship to the known dehydrating properties of phosphorus pentoxide and as will be shown by certain examples hereinafter described. The action of the phosphorus pentoxide compound apparently is more of a synergistic nature inasmuch as de-alkylation of the aromatic hydrocarbon or breaking-up of the long alkyl carbon-chain into fragments is substantially inhibited, while at the same time a catalytic substitution-influencing effect is exerted which brings about the ready entry of the sulfo-group in the ring structure to produce the desired monosulfo-aromatic compound. This dual function of the phosphorus compound manifests itself in the high yield of organic sulfonate obtained and excellent color and relative freedom from odor of the sulfonated mixture. A further advantage attained by the use of phosphoric pentoxide or phosphoric pentoxide-containing compound is that where the resultant sulfonate mixture is neutralized with alkali to form water-soluble salts thereof a certain amount of alkali phosphate is formed in situ. Such by-product phosphates particularly alkali metal phosphates viz. sodium tetraphosphate, trisodium phosphate, sodium polyphosphate, etc., are known water conditioners and are generally incorporated in varying amounts to provide improved detergency characteristics. Utilizing the process of the invention to prepare an alkylated aryl sulfonate detergent, the subsequent addition of alkali metal phosphates and the like

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inorganic builders is made unnecessary, being formed in situ during neutralization of the sulfonated mixture.

In the following table there is shown the results of a number of sulfonation runs made using alkylated toluene-type petroleum fractions supplied by different refineries and having a boiling range at atmospheric pressure between about 250° and 400° C. (50% boiling over 300° C.); and having a specific gravity of 20° C. of approximately 0.87 and a flash point in open cup of about 175° C. Fuming sulfuric acid containing 20% SO₃ was employed as the sulfonating agent, and the ratio by weight of hydrocarbons to sulfonating agent in each case was approximately 1:1. The sulfonation reaction was initiated at a temperature between 0° and 10° C. followed by the aging time and temperature shown. The control represents the average yield obtained using alkylated toluene hydrocarbon fractions as supplied by four different refineries and boiling between 250° and 400° C. as aforementioned. The percentage proportion of catalyst used is based on the weight of the hydrocarbon mixture being sulfonated.

Table 1

Run	Yield-Promoting Catalyst	Percent of P ₂ O ₅	Aging, Time and Temp.	Percent Yield
(1) (control).....			50° C. for ½ hr.	60 to 70.
(2).....	Phosphorus pentoxide.	2½	do	80.0.
(3).....	do	5	do	90.0.
(4).....	do	10	do	95.0.
(5).....	do	15	30° C. for ½ hr.	96.0.
(6).....	do	15	50° C. for ½ hr.	96.0.
(7).....	Tetraphosphoric acid* (15% by wt.).	12½	do	89.0.
(8).....	Tetraphosphoric acid* (20% by wt.).	17	30° C. for ½ hr.	94.0.
(9).....	do	17	50° C. for ½ hr.	95.0.

* Approximately 85% P₂O₅.

As the tabulated results indicate, where upwards of 5% phosphorus pentoxide is present, based on the weight of hydrocarbon being sulfonated, the sulfonation yield is on the order of 90% or better. This high yield is obtained employing only a 1:1 weight ratio of hydrocarbon to fuming sulfuric acid. In the runs made utilizing tetraphosphoric acid larger proportionate amounts of the phosphoric acid were required in order to obtain yields of 90% or more. This is believed to be due to the fact that only part of the P₂O₅ is released or otherwise made available during the sulfonation reaction to perform the desired catalytic action.

In order to compare the effect produced with phosphorus oxide catalysts with that obtained when a like amount of a different dehydrating agent is employed, additional tests were made using 15% by weight boron trioxide in place of phosphorus pentoxide. Sulfonation test runs made with boron trioxide under the same conditions as described in the above table and using 1:1 weight ratio of alkylated toluene hydrocarbon to fuming sulfuric acid gave a sulfonation yield of 63.0% on a batch sulfonated and aged at 30° C. for one-half of an hour, and a 69.0% yield on a like batch aged at 50° C. for the same period. The results thus obtained with boron trioxide indicate that the improved results produced with phosphorus pentoxide or phosphorus pentoxide-containing compounds are not primarily dependent, at least, on the dehydrating characteristic property of the compound. Further, while it has been proposed in the literature to use oxygen-containing phosphorus compounds as dehydrating agents in sulfonation processes generally, it has not been known heretofore that the sulfonation of alkylated homologues of benzene could be markedly improved with respect to the quality and yield of the organic sulfonate product produced by sulfonating in the presence of a sufficient amount of phosphorus pentoxide. The improvement is achieved employing a minimum amount of sulfonating agent by carrying out the sulfonation reaction in the presence of a relatively large proportionate amount of phosphorus pentoxide or phosphorus compound containing phosphorus pentoxide.

Additional sulfonation test runs which were carried out using in one case alkylated benzene, for example, dodecyl benzene and in another an alkylated benzene homologue,

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for example, dodecyl toluene illustrate the difficulty in obtaining good sulfonation yields with alkylated benzene homologues as compared with alkylated benzene. The following table gives the average yields produced in a number of runs. The sulfonating agent employed in each case was fuming sulfuric acid comprising 20% SO₃, and the proportion of hydrocarbon to sulfuric acid was 1:1 by weight (equal to approximately 0.36 mol of hydrocarbon to 1 mol of sulfonating agent). Aging or residence time of the sulfonated mixture was 30 minutes at 50° C.

Table 2

Hydrocarbon	Catalyst, Percent	Average Percent Yield Organic Sulfonate
Dodecyl benzene.....	None.....	95
Dodecyl toluene.....	do.....	70
Do.....	P ₂ O ₅ (10% by wt. of hydrocarbon).....	95

As the data of Table 2 indicates, there is no particular difficulty in obtaining sulfonation yields of over 90% with the alkylated benzene-type hydrocarbons. On the other hand where poly-substituted benzene compounds, such as alkylated toluene, is used the yield is poor unless sufficient phosphorus pentoxide is present during sulfonation. Using less than about 5% by weight phosphorus pentoxide, based on the weight of the hydrocarbon present however, produces yields below 90% which is usually undesired. Moreover, it has been observed that where the sulfonation of the alkylated homologues of benzene is carried out omitting the catalyst but employing larger proportionate amounts by weight of sulfuric acid, for example on the order of 1.5 to 2 parts sulfuric acid to one part hydrocarbon, the yield is increased but the sulfonated mixture is somewhat darker in color and of inferior quality as compared with the same product made using less sulfonating agent, and which sulfonation reaction is carried out in the presence of phosphorus pentoxide as described. Moreover, the use of larger than 1:1 weight proportions of hydrocarbon to sulfonating agent, as heretofore mentioned, provides a product after neutralization with alkali which contains a high proportionate amount of inorganic sulfate and a correspondingly lower percentage of organic sulfonate or active ingredient. Accordingly, where it is desired to provide a finished sulfonated product having a high proportion of active ingredient it is imperative that the excess of sulfuric acid, over that required to substantially completely sulfonate by hydrocarbon present, be kept to a minimum otherwise upon neutralization of the sulfonated mixture, the percentage amount of organic sulfonate present will be correspondingly decreased due to the increased amount of inorganic sulfate formed.

The invention is further illustrated by the following examples but it will be understood that the same is not limited thereto.

Example 1

To 200 grams of aryl alkylate (principally dodecyl toluene) having a specific gravity of 0.871 at 20° C. and boiling between about 290° and 330° C. (50% boiling over 300° C.) is added 40 grams of tetraphosphoric acid. The resultant mixture is placed in a round bottom flask equipped with a thermometer and mechanical stirrer, the flask being cooled by a methanol and Dry Ice bath, and while the temperature is kept at about 0° to 10° C., 203 grams of fuming sulfuric acid (20% SO₃) is added slowly while the mixture is stirred vigorously. After all the sulfuric acid is added the cooling bath is replaced with a warm water bath and the mixture is divided into two portions one of which is aged thirty minutes at 30° C. and the other for half an hour at 50° C. The yield of organic sulfonate at both 30° C. and 50° C. is approximately 95%.

Example 2

A portion of the aryl aromatic sulfonate prepared as described in Example 1 is neutralized with sodium hydroxide and roll-dried to produce a detergent composition containing about 50% active ingredient and 11.14% sodium phosphate, the remainder being principally sodium sulfate. The product is of light color and is sub-

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stantially free of odor, forming an excellent wetting and detergent agent.

Example 3

Two hundred grams of aryl alkylate as described in Example 1 is reacted with 203 grams of fuming sulfuric acid (20% SO_3) in the presence of 30 grams of P_2O_5 . The yield of aliquots sulfonated and aged at both 30° and 50° C. is approximately 96% of the theoretical.

Example 4

A sample portion of the sulfonate mixture prepared as described in Example 3 is neutralized with sodium hydroxide and roll-dried without extraction. The finished product contains approximately 50.60% active ingredient and 10.10% sodium phosphate, the remainder being principally inorganic sulfate. The product has excellent wetting and detergent properties and is of light color and free from undesirable odors and objectionable tackiness.

Example 5

A sulfonation run is carried out as described in Example 1 using 100 parts of aryl alkylate distillate but supplied from a different source. One hundred grams of the hydrocarbon is reacted at 0° to 10° C. with 101.5 grams of fuming sulfuric (20% SO_3), and using 40 grams of tetraphosphoric acid as the catalyst. The organic sulfonate yield upon addition of the oleum and aging at 50° C. for one-half hour is found to be 95% in this instance.

Example 6

Upon roll-drying a sample portion of the sulfonate mixture prepared as described in Example 5, which is neutralized with sodium hydroxide, a superior detergent product is provided which contains approximately 51.00% active ingredient and 14.22% sodium phosphate which is formed in situ during neutralization of the sulfonate mixture.

Instead of roll-drying the neutralized sulfonate mixtures as described, the salt mixture may be spray-dried to form a solid detergent product.

While in the above examples the sulfonating agent used is fuming sulfuric or oleum, other suitable sulfonating agents may be utilized for this purpose, for example 100% sulfuric acid, sulfur trioxide, etc. Similarly, the hydrocarbon material may comprise alkylated toluene or xylene compounds, such as the monoaryl-substituted polymers viz. propylene polymers in which the aryl substituent is a mono-nuclear hydrocarbon of toluene, xylene or the like homologue of benzene, the polymer portion being of relatively high molecular weight but preferably boiling below about 300° C. Mixtures of these hydrocarbon polymers with corresponding benzene substituted hydrocarbons are also applicable for sulfonation in accordance with the present invention.

Although the sulfonation process is preferably carried out using a 1:1 ratio by weight of alkyl aryl hydrocarbon mixture and sulfonating agent, improved results as regards yield and quality of product may be attained using slightly higher or lower proportionate amounts of the ingredients. Also where it is desired, the phosphoric acid catalyst may be introduced into the oleum prior to mixing the same with the hydrocarbon to be sulfonated or the catalyst may be introduced concurrently during addition of the sulfonating agent. The sulfonation reaction may also be carried out at higher temperatures, for example at ordinary room temperatures or above, but it is preferred that the temperature be kept below about 30° C. to obtain the best results.

The process of the invention provides an improved method of sulfonating poly-substituted aromatic compounds, viz. alkylated toluene, xylene, etc., which heretofore have been difficult to sulfonate and produce a satisfactory product of good quality, high yield and which is substantially free of odor and color bodies and unsulfonated residues. The present method makes it possible to produce superior synthetic detergent compositions of the alkyl aryl sulfonate type which comprises upwards of 50% by weight of alkyl aryl sulfonate salt or active ingredient without the necessity and expense of concentrating the alkyl aromatic sulfonic acids produced during sulfonation. Upon neutralization of the sulfonated mixture, moreover, there is produced a water-soluble salt detergent composition containing not only a high percentage amount of active ingredient but a desirable amount of

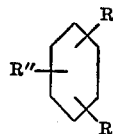
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alkali phosphate which is formed in situ, the proportion of active ingredient and phosphate salt in the mixture being on the order of 50 to 60% and 10 to 20% by weight respectively. This is in marked contrast to the ordinary production of such synthetic detergent compositions wherein the active ingredient in the neutralized mass is on the order of 35 to 40% by weight of the mixture and alkali phosphate builders, where desired, must be suitably admixed therewith. In addition, the invention provides for the utilization of less costly hydrocarbons in the production of alkyl aryl detergents, wetting agents and surface-active compositions. It is also possible to sulfonate alkylated homologues of benzene so as to obtain a yield of 95% or better, while using less proportionate amounts of the sulfonating agent than has been considered practicable heretofore in the commercial production of such aryl aromatic sulfonates.

It will be understood that various modifications and substitutions may be utilized for carrying out the process and such as will occur to those skilled in the art. Such modifications and variations are intended to be covered by the present invention, the same being limited only by the expressed limitations in the appended claims.

What is claimed is:

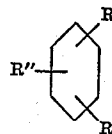
1. An improved process for sulfonating polyalkylated aromatic hydrocarbons which consists in reacting a sulfonating agent with a hydrocarbon mixture which distills between about 250° and about 400° C. and which contains principally alkylated benzene homologues of the type represented by the general formula



wherein R represents an alkyl radical which has a carbon chain corresponding to that contained in an olefin boiling between about 150° and about 275° C., R' is a short chain alkyl radical of 1 to 3 carbon atoms, and R'' is a material selected from the group consisting of hydrogen and an alkyl radical of 1 to 3 carbon atoms, said sulfonation reaction being carried out in the presence of a catalyst selected from the group consisting of phosphorous pentoxide and phosphoric acid derivatives thereof, said sulfonation reaction being carried out in the presence of only the recited materials and said catalyst being present in an amount approximating at least 5% by weight of phosphorous pentoxide based on the weight of said hydrocarbon mixture.

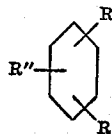
2. A process as set forth in claim 1 in which the sulfonating agent comprises fuming sulfuric acid.

3. An improved process for the monosulfonation of polyalkylated aromatic hydrocarbons comprising principally alkyl substituted homologues of benzene of the type represented by the general formula



wherein R represents an aliphatic chain of 10 to 18 carbon atoms, R' is a short chain alkyl radical of 1 to 3 carbon atoms, and R'' is a material selected from the group consisting of hydrogen and an alkyl radical of 1 to 3 carbon atoms, which consists in mixing and reacting said hydrocarbon mixture with a sulfonating agent in the presence of phosphorous pentoxide, said sulfonation reaction being carried out in the presence of only the recited materials and said phosphorous pentoxide being present in an amount approximating at least 5% by weight of said hydrocarbon mixture.

4. An improved process for the monosulfonation of polyalkylated aromatic hydrocarbons comprising principally alkyl substituted homologues of benzene of the type represented by the general formula



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wherein R represents an aliphatic chain of 10 to 18 carbon atoms, R' is a short chain alkyl radical of 1 to 3 carbon atoms, and R'' is a material selected from the group consisting of hydrogen and an alkyl radical of 1 to 3 carbon atoms, which consists in mixing and reacting said hydrocarbon mixture with a sulfonating agent in the presence of a phosphoric acid derivative of phosphorous pentoxide, said sulfonation reaction being carried out in the presence of only the recited materials and said phosphoric acid derivative being present in an amount approximating at least 5% by weight of phosphorous pentoxide based on the weight of said hydrocarbon mixture.

5. A process as set forth in claim 4 in which said phosphoric acid derivative of phosphorous pentoxide is tetraphosphoric acid.

6. An improved process for sulfonating a hydrocarbon mixture comprising an alkyl substituted toluene wherein the alkyl substituent contains about 10 to about 18 carbon atoms and has a boiling point within the range of about 150° to about 275° C., which consists in mixing and reacting said hydrocarbon mixture with sulfuric acid in the presence of a catalyst selected from the group consisting of phosphorous pentoxide and phosphoric acid derivatives thereof, said sulfonation reaction being carried out in

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the presence of only the recited materials and said catalyst being present in an amount equivalent to at least about 5% by weight of phosphorous pentoxide based on the weight of the hydrocarbon mixture being sulfonated.

7. A process for the production of alkyl aryl sulfonate detergent salts which consists in reacting a sulfonating agent with a hydrocarbon mixture consisting essentially of monoalkylated toluenes obtained by alkylating toluene with an aliphatic hydrocarbon fraction distilling within the range of about 150° to about 275° C., said reaction being carried out in the presence of a catalyst selected from the group consisting of phosphorous pentoxide and phosphoric acid derivatives thereof, said sulfonation reaction being carried out in the presence of only the recited materials and said catalyst being present in an amount approximating at least 5% by weight of phosphorous pentoxide based on the weight of said hydrocarbon mixture, and neutralizing the resultant mixture.

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