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SULFONATION OF ALKARYL HYDROCARBONS

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This invention relates to an improved process for the sulfonation of mixtures of alkaryl hydrocarbons consisting of monoalkaryl hydrocarbons and di-alkaryl hydrocarbons. More particularly this invention relates to a process for the sulfonation of such alkaryl hydrocarbons with oleum whereby sulfonic acids substantially free of sulfur dioxide and sulfuric acid are prepared.

In the production of alkaryl hydrocarbons for use as intermediates in the manufacture of surface active compounds by the alkylation of aromatic hydrocarbons with an alkylating agent there is usually formed in addition to the desired mono-alkaryl hydrocarbon more or less of a hydrocarbon fraction boiling above the boiling range of the desired components. This higher boiling hydrocarbon fraction contains a mixture of hydrocarbons most of which are mono- and di-alkaryl hydrocarbons. As for example, when benzene is alkylated with a close boiling dodecene fraction the crude product obtained is composed of (a) unreacted benzene, (b) lower disproportionation products comprising non-aromatics (naphthenes and open chain saturates) and C_2 to C_9 alkyl benzene, (c) dodecylbenzene, and (d) a substantially distillable bottoms (A.S.T.M. boiling range about 600–770° F.) which is commonly referred to as "polydodecylbenzene." Although this term is somewhat inaccurate, it will be so used in the specification and the appended claims. Actually this polydodecylbenzene consists predominantly of high molecular weight branched chain alkyl benzenes, the principal components being di-alkylated benzenes where the alkyl chain may vary from C_9 – C_{15} (both p and m isomers) or higher and mono- C_{15} – C_{24} -benzenes; the increase from charged dodecene C_{12} to C_{18} resulted from the disproportionation reactions taking place during the alkylation process. The quantity of polydodecylbenzene bottoms produced, and the relative proportions of its indicated components, have been noted to vary somewhat with the ratio of benzene to dodecene employed in the alkylation; likewise the molecular weight may vary between about 325 and 450. These constitutional variations were observed generally for ratios of benzene: C_3 polymer olefin from about 4:1 to about 10:1. The nature of the polydodecylbenzene bottoms is not expected to vary substantially from the above when employing C_3 -polymers within the range of about C_9 to C_{18} olefins in the alkylation with benzene.

Sulfonates prepared from the high boiling mixtures described above are useful for a number of purposes including lubricant detergents and corrosion inhibitors. When, however, hydrocarbons containing both mono- and di-alkaryl hydrocarbons are sulfonated, the reaction is characterized by side reactions such as splitting of the alkyl radical from the aromatic nucleus and oxidation of the hydrocarbon with the resultant formation of sulfur dioxide. Since di-alkaryl hydrocarbons are rather difficult to sulfonate, large amounts of the sulfonating agent are required in the process resulting in a high concentration of sulfuric acid in the final product.

It is, therefore, a principal object of the present invention to provide a process for the sulfonation of mixtures of alkaryl hydrocarbons which will obviate the disadvantages of the prior art processes. It is a further object of our invention to provide a process for the sulfona-

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tion of mixtures of hydrocarbons containing mono- and di-alkaryl hydrocarbons whereby the sulfonated product may be obtained in high yields and be substantially free of inorganic impurities. These and other objects will be apparent from the following description.

To the accomplishment of the foregoing and related ends this invention then comprises the features herein-after fully described and particularly pointed out in the claims, the following description setting forth in detail certain illustrative embodiments of the invention, these being indicative, however, of but a few of the various ways in which the principles of the invention may be employed.

Broadly stated, the present invention comprises a process of sulfonating alkaryl hydrocarbons whereby side reactions are held to a minimum and sulfonated alkaryl hydrocarbons are produced substantially free of sulfur dioxide and sulfuric acid comprising:

(a) Sulfonating a mixture of alkaryl hydrocarbons consisting of 25 to 90% mono- and 75 to 10% di-alkaryl hydrocarbons with an optimum quantity of oleum,

(b) Quenching the reaction mixture with an oil which is substantially unsulfonatable, and water,

(c) Allowing the quenched reaction mixture to separate into two liquid phases, an upper phase comprising the oil having dissolved therein the sulfonated alkaryl hydrocarbons and a lower phase comprising water and spent acid,

(d) Separating the two phases,

(e) Diluting the recovered upper phase with a volatile hydrocarbon,

(f) Allowing the diluted sulfonated hydrocarbons to separate into two liquid phases, an upper phase comprising said volatile hydrocarbon having dissolved therein said sulfonated alkaryl hydrocarbons and oil and a lower phase comprising spent acid and sludge,

(g) Separating the two phases, and then

(h) Removing the volatile hydrocarbon contained in said upper phase to recover therefrom the sulfonated alkaryl hydrocarbons dissolved in said oil.

Before proceeding with specific examples illustrating our invention it may be well to indicate in general the nature of and the amounts of the various materials required in the process.

Suitable alkaryl hydrocarbons may consist of various mixtures of mono- and di-alkaryl hydrocarbons within the concentration range specified above. The process of this invention is particularly applicable to products produced by the alkylation of an aromatic hydrocarbon with a poly low molecular weight olefin in the presence of an alkylating catalyst such as aluminum chloride, sulfuric acid, and catalysts of the Friedel-Crafts type.

As to the amount (X) of oleum used in the sulfonating step per part of alkaryl hydrocarbons employed, that may be expressed by the equation

$$X = 12.6_y^{-0.53} \pm 0.05$$

wherein y is equal to the weight percent of the mono-alkaryl hydrocarbons in the hydrocarbon mixture. We have found that the foregoing equation as to the amount of oleum holds true for concentrations of oleum ranging from 10 to 50 percent. Obviously a larger quantity of oleum could be used than that specified by the foregoing equation. Such a procedure is undesirable because it increases the expense of operation, side reactions, and the amount of sulfuric acid and sulfur dioxide in the sulfuric acid. The sulfonating step is carried out under sulfonating conditions of temperature and time which factors are well known to those skilled in the art and will not be discussed further.

After the completion of the oleum addition the sulfonation reaction is allowed to continue for one hour,

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after which time a volume of light oil which may vary from about .5 to 2 parts of the oil per part of alkaryl hydrocarbons is added. We prefer to employ about .9 to 1.1 parts of the oil per part of alkaryl hydrocarbons. Suitable oils are light petroleum oils which have been refined either by a solvent or a chemical process such as treatment with concentrated sulfuric acid to remove unsaturated and aromatic constituents from the oil so as to render it substantially unsulfonatable. An oil which we have found particularly useful in the process of our invention is the product known as white mineral oil or simply white oil. Another suitable oil is the product known as pale oil. These oils are added merely as diluents, consequently their actual viscosity is rather unimportant. Suitable and preferred viscosities of these oils vary from 80 to 170 and 100 to 125 SSU at 100° F. respectively. As to the amount of water added in the quenching step, that should be sufficient so that the concentration of the acid in the spent acid layer will vary from 65 to 78% calculated as sulfuric acid. Stated another way, suitable and preferred amounts of water vary from .05 to .2 and .09 to .125 part respectively per part of oleum used in the sulfonation step.

Suitable volatile hydrocarbon diluents are those having a boiling point below the decomposition temperature of the sulfonic acid. Solvents falling into this classification include the volatile aromatic and aliphatic hydrocarbons such as benzene, toluene, the xylenes and liquid aliphatic hydrocarbons containing up to 7 carbon atoms. Of these two types of suitable volatile hydrocarbons, we prefer the aromatics, as the aromatic hydrocarbons serve two purposes, they aid in the further removal of inorganic acidic materials and the removal of undesirable acidic materials as a sludge which settles out of the aromatic diluted sulfonic acid-white oil solution. As to the amount of the volatile aromatic hydrocarbon diluent used, that is not critical but may vary from about 1.5 to 9 times the volume of the sulfonic acid. Based on the amount of sulfonic acid-white oil solution, the volume of the aromatic hydrocarbon used may vary from about 1 to 3 times the volume of the sulfonic acid-white oil solution.

The sulfonates produced by our process are particularly desirable as oil additives because they, including those where the cation is an alkaline earth metal, are compatible with oil.

In order to disclose the nature of the present invention still more clearly, the following illustrative examples will be given in which parts are parts by weight.

EXAMPLE 1

A reaction vessel was charged with 445 parts of benzene, 0.1 part of water, and 8 parts of commercial grade anhydrous aluminum chloride. Into this mixture was then added, during 30 minutes, 252 parts of propene tetramer and at 15 minute intervals 4 parts of aluminum chloride. During the addition, the temperature rose from 26° C. to 55–60° C. The mixture was agitated for 15 minutes and then treated with 100 parts of 5% sodium hydroxide. The crude organic portion was separated and fractionated through a column having nine theoretical plates. There was obtained 335 parts of benzene, 44 parts of a fraction boiling 60–121° C./20 mm., 211 parts of dodecylbenzene boiling 121–216° C./20 mm. and 71 parts of still bottoms (polydodecylbenzene) having the following characteristics:

A.S.T.M., D-158 Engler, boiling point:

I.B.P. -----	°F--	647
5% -----	°F--	682
50% -----	°F--	715
90% -----	°F--	760
95% -----	°F--	775
F.B.P. -----	°F--	779
Specific gravity, 74° F. -----		0.8649
Apparent molecular weight -----		365

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Bromine number -----	0.50
Aniline point -----	°F-- 156
Refractive index, 74° F. -----	1.4900
Flash point (c.o.c.) -----	°F-- 381
Viscosity, S.S.U., 200° F. -----	57
Percent aromatics -----	99
Percent monoalkyl aromatics -----	31

EXAMPLES 2-4

The procedure of Example 1 was repeated with the exception that the amount of benzene used was changed. The amount of benzene and the mole percent of monoalkylaryl hydrocarbon present in the product are given in Table 1.

Table 1

COMPOSITION OF PRODUCT FOR VARIOUS MOLE RATIOS OF BENZENE TO DODECENE

Example No.	Amount of Benzene	Ratio of Benzene to Dodecene	Composition of Product Mole Percent Monoalkyl Aryl Hydrocarbon
1-----	445	3.8/1	31
2-----	515	4.4/1	42
3-----	760	6.5/1	54
4-----	1,170	10/1	78

EXAMPLES 5-28

In a series of reactions the still bottoms products of Examples 1, 2, 3, and 4 boiling above 216° C./20 mm. (corresponding to 360° C./atm.) were sulfonated with various amounts of 20% oleum. The oleum was added during 30 minutes while the mixture was maintained at 60° C. The mixture was then agitated for an additional hour at 60° C. There was then added 175 parts of white oil to quench the reaction. Agitation was discontinued and the mixture allowed to settle for 72 hours at 45° C. The lower acid layer was withdrawn and the upper crude sulfonic acid diluted with 700 parts of benzene. The resulting mixture was agitated to mix and then allowed to settle for 18 hours. The lower acid layer that separated was withdrawn and the upper benzene layer was degassed by distilling off the benzene. Table 2 gives the efficiency of sulfonation as measured by the concentration of the sulfonic acid in the sulfonation mixture for various amounts of oleum.

Table 2

SULFONATION OF ALKYLARYL HYDROCARBONS CONTAINING VARIOUS AMOUNTS OF MONOALKYLARYL HYDROCARBON WITH 20% OLEUM

Ex. No.	Percent Monoalkylaryl Hydrocarbon in Hydrocarbon being Sulfonated	Parts of Oleum Per Part of Hydrocarbon	Concentration of Sulfonic Acid in Product, meg./g.	Ratio of Sulfuric to Sulfonic Acid in Product
5-----	31	1.00	0.89	5.0
6-----	31	1.25	1.00	5.1
7-----	31	1.50	1.06	5.5
8-----	31	1.70	1.12	6.0
9-----	31	2.00	1.14	6.5
10-----	31	2.25	1.15	7.0
11-----	42	1.00	0.95	5.4
12-----	42	1.25	1.09	7.2
13-----	42	1.50	1.15	6.6
14-----	42	1.75	1.19	7.0
15-----	42	2.00	1.20	11.6
16-----	42	2.25	1.21	13.3
17-----	54	1.00	1.00	7.5
18-----	54	1.25	1.13	8.5
19-----	54	1.50	1.19	9.0
20-----	54	1.75	1.21	10.5
21-----	54	2.00	1.22	12.0
22-----	54	2.25	1.22	12.3
23-----	78	0.50	0.74	5.2
24-----	78	0.75	1.03	6.0
25-----	78	1.00	1.17	7.0
26-----	78	1.25	1.24	10.3
27-----	78	1.50	1.28	13.5
28-----	78	1.75	1.29	14.0

¹ Total inorganic acidity of product expressed as sulfuric acid.

These data reveal that optimum yields of sulfonic acid are obtained by the sulfonation of mixtures of alkylaryl hydrocarbons when the mixture is sulfonated with the following amounts of 20% oleum or its equivalent, depending on the concentration of mono-alkylaryl hydrocarbon in the mixture.

Table 3

Cone. of Monoalkylaryl Hydrocarbon in the Hydrocarbon Mixture—Percent Mono-	Amount of 20% Oleum Required for Optimum Yields of Sulfonic Acid—Parts 20% Oleum/Part of Hydrocarbon
31-----	2.00
42-----	1.75
54-----	1.50
78-----	1.25

The data of Table 3 may be expressed by the relationship:

$$X=12.6_y^{-0.53}\pm 0.05$$

wherein X and y are as identified above.

In another series of reactions the still bottoms products of Examples 1, 2, 3, and 4 boiling above 216° C./20 mm. were sulfonated with various amounts of 20% oleum as described in Examples 5 through 28. The products of these sulfonations, however, were quenched with various amounts of water in addition to the 175 parts of white oil. The amount of sulfuric acid remaining in the product decreased with increasing amounts of water up to about 0.125 part of water per part of oleum. When more than 0.125 part of water are used, separation of spent acid becomes difficult and impractical.

The procedure of Examples 5-28 were repeated with the exception that 175 parts of 170 SSU pale oil at 100° F. were substituted for the 175 parts of white oil. The results obtained were similar to those obtained in Examples 5 to 28.

While particular embodiments of the invention have been described, it will be understood, of course, that the invention is not limited thereto since many modifications may be made, and it is, therefore, contemplated to cover by the appended claims any such modifications as fall within the true spirit and scope of the invention. As for example, an alternate, but a less preferred procedure, the volatile aromatic hydrocarbon solution of the sulfonic acid may be degassed by blowing with air or other gas which will not react with the sulfonic acid or other constituents present in the solution. Such a procedure is generally unnecessary as all the sulfur dioxide contained in the solution will be removed before all the volatile aromatic hydrocarbon has been removed.

The invention having thus been described, what is claimed and desired to be secured by Letters Patent is:

1. A process for the production of oil soluble sulfonated alkyl substituted benzenes substantially free of sulfur dioxide and sulfuric acid which comprises: (a) the sulfonation of a mixture of alkyl substituted benzenes consisting of 25 to 90% mono-alkyl substituted benzenes and 75 to 10% di-alkyl substituted benzenes with oleum wherein the parts (X) of oleum per part of alkyl substituted benzenes employed may be expressed by the equation

$$X=12.6_y^{-0.53}\pm 0.05$$

wherein y=weight percent of the mono-alkyl substituted benzenes in said hydrocarbon mixture, (b) quenching the reaction mixture with 0.5 to 2.0 parts of a light petroleum oil refined by a process to remove therefrom unsaturated and aromatic constituents per part of alkyl substituted benzenes and 0.05 to 0.2 part of water per part of oleum

used in (a), (c) allowing the quenched reaction mixture to separate into two liquid phases, an upper phase comprising the light petroleum oil having dissolved therein the sulfonated alkyl substituted benzenes and a lower phase comprising water and spent acid, (d) separating the two phases, (e) diluting the recovered upper phase with a volatile aromatic hydrocarbon wherein the volume of the aromatic hydrocarbon diluent is equal to 1.5 to 9 times the volume of the alkyl substituted benzenes, (f) allowing the diluted sulfonated substituted benzenes to separate into two liquid phases, an upper phase comprising said aromatic hydrocarbon diluent having dissolved therein said sulfonated alkyl substituted benzenes and light petroleum oil and a lower phase comprising spent acid and sludge, (g) separating the two phases, and then (h) removing the volatile aromatic hydrocarbon contained in said upper phase to recover therefrom the sulfonated alkyl substituted benzenes dissolved in said light petroleum oil.

2. A process for the production of oil soluble sulfonated alkyl substituted benzenes substantially free of sulfur dioxide and sulfuric acid which comprises: (a) the sulfonation of a mixture of alkyl substituted benzenes consisting of 25 to 90% mono-alkyl substituted benzenes and 75 to 10% di-alkyl substituted benzenes with oleum wherein the parts (X) of oleum per part of alkyl substituted benzenes employed may be expressed by the equation

$$X=12.6_y^{-0.53}\pm 0.05$$

wherein y=weight percent of the mono-alkyl substituted benzenes in said hydrocarbon mixture, (b) quenching the reaction mixture with 0.9 to 1.1 parts of a light petroleum oil refined by a process to remove therefrom unsaturated and aromatic constituents per part of alkyl substituted benzenes and 0.09 to 0.125 part of water per part of oleum used in (a), (c) allowing the quenched reaction mixture to separate into two liquid phases, an upper phase comprising the light petroleum oil having dissolved therein the sulfonated alkyl substituted benzenes and a lower phase comprising water and spent acid, (d) separating the two phases, (e) diluting the recovered upper phase with a volatile aromatic hydrocarbon wherein the volume of the aromatic hydrocarbon diluent is equal to 1.5 to 9 times the volume of the alkyl substituted benzenes, (f) allowing the diluted sulfonated substituted benzenes to separate into two liquid phases, an upper phase comprising said aromatic hydrocarbon diluent having dissolved therein said sulfonated alkyl substituted benzenes and light petroleum oil and a lower phase comprising spent acid and sludge, (g) separating the two phases, and then (h) removing the volatile aromatic hydrocarbon contained in said upper phase to recover therefrom the sulfonated alkyl substituted benzenes dissolved in said unsulfonatable oil.

3. The process of claim 1 wherein the mixture of alkyl hydrocarbons is polydodecylbenzene.

4. The process of claim 1 wherein the light petroleum oil is pale oil.

5. The process of claim 1 wherein the light petroleum oil is white oil.

6. The process of claim 1 wherein the volatile aromatic hydrocarbon is benzene.

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