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METHOD OF PREPARING OIL SOLUBLE SULFONATES

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This invention relates to an improved process for the production of oil soluble alkyl benzene sulfonates from a mixture of alkyl benzenes. More particularly this invention relates to a process whereby light colored oil soluble alkyl benzene sulfonates are produced which are substantially free of oil insoluble alkyl benzene sulfonates.

In the production of alkyl benzenes for use as intermediates in the manufacture of surface active compounds by the alkylation of benzene with an alkylating agent there is usually formed in addition to the desired compounds more or less of alkyl benzenes boiling above and below the boiling range of the desired components. As for example, when benzene is alkylated with a close boiling dodecene fraction the crude product obtained is composed of:

(*a*) Unalkylated benzene,

(*b*) Lower disproportionation products comprising non-aromatics (naphthenes and open chain saturated) and C_6 to C_9 alkyl benzene,

(*c*) Dodecylbenzene, and

(*d*) A substantially distillable bottoms (A.S.T.M. boiling range about 600 to 780° F.) which is commonly referred to as crude postdodecylbenzene. Although this term is somewhat inaccurate, it will be so used in the specification and in the appended claims.

Actually, crude postdodecylbenzene consists predominately of high molecular weight branch chain alkyl benzenes. The principal components being dialkylated benzenes where the alkyl chain may vary from C_9 to C_{15} (both para and meta isomers) or higher, and mono C_{15} to C_{24} benzenes. The quantity of crude postdodecylbenzene 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 step. Likewise, the molecular weight may vary between 275 and 450. In addition, the actual process employed in the alkylation step and the method of operating the distillation step will cause a variation in the properties of the postdodecylbenzene.

Sulfonates prepared from postdodecylbenzene and similar fractions are useful for a number of purposes including lubricant detergents, corrosion inhibitors, detergent compositions, emulsifiers and similar uses. In many cases the sulfonates are objectionable because of color and they are not completely oil soluble. In general, the color of the product may be improved by carrying out all of the reaction in the presence of glass or a similar non-reactive material such as stainless steel. The production of a product which is completely oil soluble has been exceedingly difficult by the prior art processes. It has been known that sulfonates prepared from mixtures of alkyl benzenes such as postdodecylbenzene are composed of high molecular weight sulfonates which are oil soluble, plus certain quantities of low molecular weight sulfonates which are oil insoluble. The presence of these latter compounds has been the cause of the difficulty. Attempts have been made to eliminate these low molecular weight sulfonates including fractional distillation whereby the

first fraction during the distillation step is discarded. This has been only partially successful because it has been very difficult to strip out the low boiling components by distillation, and secondly, low molecular weight sulfonic acids are produced during sulfonation.

It is, therefore, a principal object of the present invention to provide a process whereby alkyl benzene sulfonates may be produced from mixtures of alkyl benzenes using sulfuric acid or oleum as the sulfonating agent which will obviate the disadvantages of the prior art processes. It is a further object of our invention to provide a process whereby oil soluble alkyl benzene sulfonates may be produced which are light colored and substantially free of low molecular weight alkyl benzene sulfonates. 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 hereinafter 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.

Briefly stated, we have found that oil soluble sulfonates of good color and quality may be prepared from a mixture of alkyl benzenes by a process involving sulfonation followed by a batch solvent extraction step using as a solvent a relatively large volume of an oil which is substantially unsulfonatable whereby spent sulfuric acid, oil insoluble sulfonic acids, and color precursors are removed from the unsulfonated alkyl benzenes and oil soluble sulfonic acids.

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 components required in the process.

As mentioned above, the product known as crude postdodecylbenzene is suitable and, dependent upon the operating and recovery conditions used in the preparation of this product, the molecular weight may vary from about 275 to 450. Generally, the crude postdodecylbenzene is subjected to fractional distillation whereby the product known as dodecylbenzene is removed as the overhead distillate. The residue known as stripped postdodecylbenzene, or more simply, as postdodecylbenzene is a mixture of mono-alkyl benzene and di-alkyl benzenes in the approximate ratio of 2:3. Its typical physical properties are as follows:

Specific gravity at 38° C.	0.8649
Average molecular weight	385
Percent sulfonatable	88
A.S.T.M. .D–158 Engler:	
I.B.P.	647° F.
5	682° F.
50	715° F.
90	760° F.
95	775° F.
F.B.P.	779° F.
Refractive index at 23° C.	1.4900
Viscosity at:	
−10° C.	2800 centipoises
20° C.	280
40° C.	78
80° C.	18
Aniline point	69° C.
Pour point	−25° F.

Either concentrated sulfuric acid or oleum may be used as the sulfonating agent. Since sulfonation procedures using either of these compounds is well known to those skilled in the art, and, furthermore, since such methods

are fully described in the literature, they will not be described here.

Following the sulfonation step, the reaction mixture is diluted with an oil which is substantially unsulfonatable in an amount which may vary from about 3 to 7 parts of oil per part of the alkyl benzenes. We prefer to employ about 4 to 6 parts of the oil per part of the alkyl benzenes. Suitable oils are light petroleum oils which have been refined by either a solvent or a chemical process such as treatment with oleum 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. The oil serves two functions. It acts as diluent and causes the separation of the color precursors and low molecular weight sulfonic acids from the high molecular weight sulfonic acids and unsulfonated alkyl benzenes. Treatment of the sulfonated mixture with the white oil causes the formation of two liquid phases. The upper phase comprises the white oil having dissolved therein the oil soluble sulfonic acids and the lower phase comprises the spent acid having dissolved therein the oil insoluble sulfonic acids and the color precursors. Suitable and preferred viscosity of the white oil may vary from 70 to 170 and 80 to 100 S.S.U. at 100° F. respectively. For optimum color and quality of the final oil soluble sulfonate it is necessary to remove the oil insoluble sulfonic acids and color precursors before neutralizing the sulfonic acids or the addition of an inert solvent such as hexane to the mixture. Furtheremore, it is imperative that the foregoing separation be performed quickly; less than 24 hours. While we do not wish to be bound by any theory, we believe that the the correct explanation of these results is substantially as follows: Although the oil insoluble sulfonic acids and color precursors are initially preferentially dissolved in the spent acid layer as compared to the white layer, this solubility distribution between the two layers changes with time. As a result, if the two layers are not separated within 24 hours, a large quantity of the two impurities becomes dissolved in the white oil layer and remains as contaminants in the oil soluble sulfonic acids upon subsequent treatment. Rapid separation of the spent acid from the sulfonic acid is aided by oil dilution, solvent dilution, or centrifugation.

Following the treatment of the reaction product with the unsulfonatable oil and the separation of the two liquid phases thus formed, the upper phase comprising the unsulfonatable oil having dissolved therein the high molecular weight alkyl benzene sulfonic acids is treated with an activated earth. Suitable activated earths include bauxite, magnesol, attapulgus clay, etc.

In order to disclose the nature of the present invention still more clearly the following illustrative examples will be given. It is to be understood, however, that the invention is not to be limited to the specific conditions or details set forth in these examples except in so far as such limitations are specified in the appended claims. Parts given are parts by weight.

Example 1

Twenty parts of postdodecylbenzene was added to a reactor equipped with means for heating and cooling, an agitator, and means for adding sulfuric acid or oleum thereto. Sixteen parts of 20 percent oleum was then added to the reactor over a period of one hour. During the sulfonation reaction the temperature of the reaction mixture was maintained within the range of 150–160° F. At the end of the sulfonation reaction 100 parts of white oil of a viscosity of 100 S.S.U at 100° F. was added to the reaction mixture, transferred to a second reactor, stirred for a period of 5 minutes at a temperature of 110–120° F., and then allowed to settle for 2 hours. Two layers were formed, an upper layer comprising oil soluble sulfonic acids (postdodecylbenzene sulfonic acid) and unreacted postdodecylbenzene dissolved in the white oil and a lower layer comprising oil insoluble sulfonic acids and color precursors dissolved in the spent acid. The upper layer was removed, 13 parts of Dicalite Superoid added thereto, blown with nitrogen gas to remove dissolved gases such as SO_2 and SO_3 for a period of 30 minutes and then filtered to remove the Dicalite. Twenty parts of methanol were added to the filtrate, the resulting mixture agitated and then allowed to settle. Two layers were formed, an upper layer comprising the unreacted postdodecylbenzene dissolved in the white oil and a lower layer comprising the oil soluble sulfonic acids dissolved in the methanol. The lower layer is removed and the sulfonic acid recovered therefrom as a residue by evaporating off the methanol. The recovered sulfonic acid residue analyzed 87 percent active. The sulfonic acid is neutralized using any one of a wide variety of bases. Suitable bases include: alkali metal hydroxides, particularly sodium or potassium hydroxide, or ammonium hydroxide, or mixtures thereof are particularly suitable although alkaline earth metal hydroxides such as calcium and magnesium hydroxides, or organic bases such as amines, including alkanolamines, such as the ethanolamines, morpholine and the like may also be used. Usually the sulfonic acid is reduced to an activity of about 60 percent if the product is to be neutralized with an alkali metal base and to activity of about 30 to 40 percent if neutralized with an alkaline earth metal base. In either case the neutralized product is a light amber colored oil soluble fluid and is suitable as a motor oil detergent or can be used in the preparation of such detergents.

The white oil layer containing nonreacted postdodecylbenzene obtained as the upper layer from the methanol treatment is treated with an additional quantity of oleum to sulfonate the unreacted hydrocarbon and remove any color or color precursors picked up during the first cycle. Following this treatment the white oil can be reused.

Example 2

The procedure of Example 1 was repeated with the exception that various quantities of white oil were used in diluting the reaction mixture of postdodecylbenzene and oleum. The results are summarized in tabular form below.

Ratio parts of White Oil: Postdodecylbenzene	Acid Ratio	
	As Is	After Centrifuging
1:1	35.5	
3:1	22.2	17.9
5:1	13.0	6.6
7:1	12.2	2.9

Acid ratio is equal to percent sulfuric acid divided by percent sulfonic acid times 100. We were unable to obtain any improvement in the acid ratio by centrifuging the 1:1 sample. When 1 part of white oil is used per part of postdodecylbenzene the mixture must settle for 3 or 4 days.

Example 3

In order to provide a comparison as to the oil soluble content of the product made by the process of our invention and that made by the conventional process, the following experiment was run.

A sample of sodium sulfonate produced in accordance with this process was divided into oil-soluble and oil-insoluble fractions by means of a solvent extraction technique which involves the fractional extraction of successively lower molecular weight components from a methanolic solution of the sulfonate. Using the same

technique a sample of sodium sulfonate produced by the conventional process was divided into oil-soluble and oil-insoluble fractions. The results are summarized in tabular form below.

Process	Oil Solubility
Oil dilution	99.5% Soluble.
Conventional	81.3% Soluble.

While the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention as those skilled in the art will readily understand. As for example, the invention is illustrated specifically using synthetic sulfonic acids. It is equally applicable, however, to processes involving natural sulfonic acids.

Upon the other hand, there are certain processing steps which must be followed in order to produce alkyl aryl sulfonates of excellent quality and color. The steps which can not be altered are: dilution of the sulfonic acid mixture with 3–7 parts of a light mineral oil that is substantially unsulfonatable per part of the alkyl benzenes. This dilution step must precede neutralization. After diluting the sulfonic acid mixture with the oil the two liquid layers must be separated quickly. The specific embodiments described are given by way of examples only, and the invention is limited only by the terms of the appended claims.

We claim:

1. A process for the production of light colored oil soluble alkyl benzene sulfonates substantially free of oil insoluble alkyl benzene sulfonates from a mixture of alkyl benzenes which comprises: sulfonating said mixture of alkyl benzenes with a sulfonating agent selected from the group consisting of sulfuric acid and oleum under sulfonating conditions, diluting the resulting reaction mixture with 3 to 7 parts of a white oil, having a viscosity varying from 70 to 170 SSU at 100° F., per part of said mixture of alkyl benzenes, allowing the diluted reaction mixture to separate into two liquid phases, an upper phase comprising said white oil having dissolved therein oil soluble alkyl benzene sulfonic acids and unsulfonated alkyl benzenes and a lower phase comprising spent sulfuric acid, oil insoluble alkyl benzene sulfonic acids and color precursors, removing the lower phase from the upper phase within 24 hours, blowing the upper phase with an inert gas to remove SO_2 and SO_3 therefrom, treating the upper phase with an activated earth type filter aid, filtering the upper phase to remove said filter aid, diluting the upper phase with about one part of methanol per part of alkyl benzenes, allowing the methanol diluted upper phase to separate into two liquid phases, a lower phase comprising the methanol having dissolved therein the oil soluble alkyl benzene sulfonic acids, and an upper phase comprising said white oil having dissolved therein the unsulfonated alkyl benzenes, separating the phases, removing the methanol from the lower phase to obtain therefrom the alkyl benzene sulfonic acids, and then neutralizing the alkyl benzene sulfonic acids.

2. A process for the production of light colored oil soluble alkyl benzene sulfonates substantially free of oil insoluble alkyl benzene sulfonates from a mixture of alkyl benzenes which comprises: sulfonating said mixture of alkyl benzenes with a sulfonating agent selected from the group consisting of sulfuric acid and oleum under sulfonating conditions, diluting the resulting reaction mixture with 4 to 6 parts of a white oil, having a viscosity varying from 80 to 100 SSU at 100° F., per part of said mixture of alkyl benzenes, allowing the diluted reaction mixture to separate into two liquid phases, an upper phase comprising said white oil having dissolved therein oil soluble alkyl benzene sulfonic acids and unsulfonated alkyl benzenes and a lower phase comprising spent sulfuric acid, oil insoluble alkyl benzene sulfonic acids and color precursors, removing the lower phase from the upper phase within 24 hours, blowing the upper phase with an inert gas to remove SO_2 and SO_3 therefrom, treating the upper phase with an activated earth type filter aid, filtering the upper phase to remove said filter aid, diluting the upper phase with about one part of methanol per part of alkyl benzenes, allowing the methanol diluted upper phase to separate into two liquid phases, a lower phase comprising the methanol having dissolved therein the oil soluble alkyl benzene sulfonic acids, and an upper phase comprising said white oil having dissolved therein the unsulfonated alkyl benzenes, separating the phases, removing the methanol from the lower phase to obtain therefrom the alkyl benzene sulfonic acids, and then neutralizing the alkyl benzene sulfonic acids.

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