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METHOD FOR THE PRODUCTION OF OIL-SOLUBLE SULFONATES FROM POLYALKYLATED AROMATIC RESIDUES

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The present invention relates to new and useful improvements in substantially oil-soluble sulfonates from polyalkylated aromatic residues.

In the conventional alkylation of aromatic hydrocarbons for the production of substantially water-soluble synthetic detergents of the alkyl aryl sulfonate type, more than one alkyl radical and/or fragments thereof will frequently attach to an aromatic ring, thus producing a crude alkylation product of varied structure or composition. This necessitates a distillation of the crude alkylation product, wherein the polyalkylated aromatics remain as still bottoms.

These still bottoms, particularly those having a mean molecular weight of more than 300, have been in the past treated by sulfonation in conventional manner with, for instance, concentrated sulfuric acid and/or oleum, followed by removal of spent acids and sludge and neutralization with a suitable base to thereby obtain substantially oil-soluble sulfonates, closely resembling the valuable petroleum mahogany sulfonates derived from the acid refining of petroleum lubricating oil fractions under sulfonating conditions.

Alkyl aryl sulfonates possessing a molecular weight and structure of the order of magnitude of dodecylbenzene sulfonate are today a major source of the aforementioned water-soluble detergents, and correspondingly, the still bottoms remaining when the crude dodecylbenzene alkylation product is distilled have likewise become a major source of synthetic oil-soluble sulfonates.

For the purposes of this application, these still bottoms are hereinafter referred to generally as "dodecylbenzene still bottoms," it being understood that by this designation is meant the mixture of polyalkylated aromatics, having a mean molecular weight of above 300, which are left behind as still bottoms when a crude dodecylbenzene alkylation product is distilled, in order to obtain substantially water-soluble alkyl aryl sulfonates.

In the conventional sulfonation of these dodecylbenzene still bottoms with, for example, concentrated sulfuric acid and/or oleum, the viscosity of the reaction mixture undergoes a marked increase as the sulfonation reaction approaches completion. This viscosity increase, which impedes handling of the product and is also highly detrimental with respect to separation and removal of spent sulfuric acid and acid sludge, serves to lower the quality of the final sulfonation product and is due, at least to some extent, to the high concentration of sulfonic acids present in the reaction mix.

One object of the present invention is the production of a sulfonated product from dodecylbenzene still bottoms without a deleterious increase in the viscosity of the reaction mixture. A further object of the instant invention is the avoidance of cloudiness and/or turbidity in the sulfonation product obtained from dodecylbenzene still bottoms.

These and still further objects of the invention will become apparent from the description thereof as follows:

In accordance with the instant invention, dodecylbenzene still bottoms are initially blended with a suitable petroleum lubricating oil fraction having a Saybolt viscosity at 100° F. of 30–700 sec. The blend should contain from 40–80% by weight of dodecylbenzene still bottoms to 20–60% by weight of the petroleum lubricating oil fraction. The preferred proportion of the blend depends in each case upon the percentage of sulfonates desired from the final product.

Examples of typical distillates falling within the scope of this invention are, for example, characterized by a Saybolt viscosity at 100° F. of from 70–530, an ASTM pour point of −20° F. to +15° F., a refractive index at 20° C. of 1.47–1.50, and a sp. gr. 60° F./60° F. of 0.86–0.90. When distillates having Saybolt viscosities at 100° F. of from 30 to 700 are employed, correspondingly lower or higher physical constants, normally consonant with such viscosities as the case may be, may be used.

The sulfonation of these blends of dodecylbenzene still bottoms and petroleum lubricating oil fractions is carried out in the conventional manner hitherto practiced for such still bottoms, i. e., with concentrated sulfuric acid and/or oleum, in a batch or continuous operation, the amount of acid to be used being dependent upon the proportion of dodecylbenzene still bottoms to be treated in the composite blend, the reaction being preferably carried out so as to react substantially all of the dodecylbenzene still bottoms present.

The blend of dodecylbenzene still bottoms and petroleum lubricating oil fractions shows upon sulfonation a markedly lower viscosity than that of a product obtained by separately sulfonating (under otherwise identical conditions) the components of the blend and thereafter blending the sulfonated materials. The lower viscosity reaction mix obtained in accordance with the invention thus permits the settling and/or separation of spent acid and acid sludge with comparatively little difficulty and obviates the necessity for the use of such expedients as diluents, distillation, and/or extraction in order to overcome the viscosity difficulties normally inherent in the reaction mix from the conventional still bottom sulfonation. The presence of the petroleum lubricating oil fraction thus exerts a synergistic action, one effect of which produces a viscosity in the reaction mix lower than that which should be expected as the result of any diluent action which might be possessed by the lubricating oil fraction alone.

Another effect of the procedure in accordance with the invention is that the lubricating oil component prevents turbidity in the finished sulfonated product as such or on standing.

A further effect in accordance with the invention is the fact that the addition of the petroleum lubricating oil fraction modifies the reaction to such an extent that an increased yield of the desired oil-soluble sulfonates is obtained. This yield is larger than the aggregate which should be expected from the dodecylbenzene still bottoms and the petroleum lubricating oil fraction taken alone.

A still further effect of the reaction between the components in the practice of the invention is the fact that the molecular weight of the final product in many instances is somewhat higher than the respective molecular weights which should be obtained from the separate sulfonation of the dodecylbenzene still bottom components on the one hand, and the petroleum fraction component on the other, with a subsequent blending of final products. It is actually possible by the novel procedure to vary the molecular weight of the final product within limits by choosing different types of petroleum lubricating oil components in the reaction. Thus, for ex-

ample, where a product with a higher molecular weight is desired, a lube oil normally producing higher molecular weight sulfonates is employed, and correspondingly, where a relatively lower molecular weight product is desired, the chosen oil is one normally yielding lower molecular weight sulfonates.

The petroleum lubricating oil fraction is preferably a raffinate, obtained by conventional solvent extraction refining of petroleum oil distillates. The solvents in such a case could be, for example, any one or a mixture of the following: dichlorethylene, nitrobenzene, furfural, mixtures of benzol and phenol, and a mixture of liquid sulfur dioxide and benzol. The raffinate is preferred since it will require less effort and will form less spent acids, acid sludge, and coloring matter than would be the case if an unrefined distillate were employed.

For best results, the preferred petroleum lubricating oil fraction is one which has been partially sulfonated to contain mahogany petroleum sulfonic acids. When employing such a fraction, it is possible to appreciably reduce the amount of spent acid and acid sludge formed in the sulfonation reaction of the still bottoms blend, treated according to the invention.

The lubricating oil fraction employed should be at all times sulfonatable under conventional conditions of petroleum refinery sulfonation to produce mahogany type sulfonates to the extent of at least 1–3% by weight of said fraction. In the event a partially sulfonated lubricating oil fraction is employed, the same must be capable of producing at least approximately 10% by weight of the total oil-soluble sulfonates obtainable from the original lube oil fraction, i. e., the original lube oil fraction is partially sulfonated not exceeding substantially 90% by weight of total sulfonatables therein. A petroleum lubricating oil fraction as such, being normally a low sulfonatable petroleum oil material, may contain, for example, approximately a 10% sulfonatable content, i. e., one capable of producing approximately 10% by weight of oil-soluble sulfonates calculated as dry sodium sulfonate. The same may, however, possess an appreciably lower sulfonatable content as, for example, as low as 1–3%.

The final product obtained in accordance with the invention is a concentrated mixed sulfonic acid which, after suitable purification in conventional manner, as for example by blowing out free SO_2 and removing free H_2SO_4, by contacting with, for example, diatomaceous earth, followed by a filter-pressing operation, may be neutralized with any desired base such as NaOH. The ultimate sulfonates resulting after neutralization will remain clear upon standing without turbidity or cloudiness.

The following examples are furnished by way of illustration and not limitation:

Example 1

A sample of dodecylbenzene still bottoms having the following physical properties:

Sp. gr. 60° F./60° F.	.8800
Sayb. vis. at 100° F.	385
Sayb. vis. at 210° F.	48.5
ASTM pour point	−20
Refr. index/20° C.	1.4921

was treated with four separate dumps of oleum calculated as 104.5% H_2SO_4. The four separate dumps contained equal amounts by weight of the oleum, i. e., 25% by weight in each dump, and the sulfonation was carried out with vigorous mechanical stirring. After each dump of oleum, the reaction mixture was agitated for an hour. Thereafter, the reaction mixture was permitted to settle overnight at 120–130° F. and the acid sludge was drawn off and discarded. The sulfonic acid layer obtained in this manner had a Saybolt viscosity at 100° F. of 13,556. The crude soap produced upon neutralization of this layer with caustic soda solution and after removal of the aqueous layer and dehydration, contained a yield of sulfonic acid, expressed as dry sodium sulfonate, equivalent to 81.3% by weight with respect to the dodecylbenzene still bottoms starting product. The sulfonate had an average molecular weight of 443, was readily soluble in mineral oils and in most respects followed the behavior pattern of a sodium petroleum mahogany soap.

Example 2

A West-Texas neutral distillate obtained from an Ordovician crude having the following physical properties:

Sayb. visc. at 100° F.	73
Sp. gr. 60° F./60° F.	.8670
ASTM pour point	+15
Refr. index at 20° C.	1.4834

was treated with mechanical stirring for 10 minutes at room temperature with 10% of its weight of 66° Bé. sulfuric acid, thereafter the distillate was treated with four equal dumps, each 10% by weight of the distillate, of oleum calculated at 104.5% H_2SO_4. The reaction mixture was allowed to settle overnight after each acid dump and separated from the formed sludge. The acid treated oil was neutralized with 15% sodium hydroxide and extracted with 30% by volume of 50% aqueous alcohol. The sodium petroleum mahogany soap was contained in the alcohol layer and, after separation and evaporation, the alcohol layer yielded a crude mahogany soap containing 4.2% by weight of dry sodium sulfonate, calculated on the original neutral distillate employed. This dry sodium sulfonate had an average molecular weight of 420.

The neutral distillate remaining after extraction with aqueous alcohol was treated with acid to the extent of the single 10% by weight dump of the 66° Bé. sulfuric acid and two 20% by weight dumps of the oleum calculated as 104.5% H_2SO_4. 25.9% by weight of the resulting partly acid-treated neutral distillate was combined with 74.1% by weight of the dodecylbenzene still bottom sample employed in Example 1. A total of 84% by weight of the oleum calculated as 104.5% H_2SO_4 was added to the reaction mixture in four equal dumps in the manner described in Example 1.

The sulfonic acid layer obtained in this manner had a Saybolt viscosity at 100° F. of 627 as compared to the 13,556 of Example 1. The product obtained upon neutralization and dehydration of this layer corresponded to a sodium sulfonate, having an average molecular weight of 442 and the yield of sulfonate was 66.3% by weight of the starting blend composed of dodecylbenzene still bottoms and partly acid-treated oil.

Of this 66.3% by weight yield, 60.2% by weight would be normally obtained from the dodecylbenzene still bottoms alone; this figure is arrived at by multiplying the weight percentage of dodecylbenzene employed in the blend (74.1%) by 81.3, i. e., the percent by weight yield where the dodecylbenzene still bottom sample was used alone as in Example 1. Similarly, since 25.9 parts by weight of partly acid-treated oil of this example (which gave a percent by weight yield of 4.2) were employed in the starting blend, the yield of sodium sulfonate (calculated dry) which should be normally obtained from this quantity of acid treated oil alone, is 1.1% by weight. Thus, the total sulfonate yield from the blend is 5% by weight higher than the yield obtained by sulfonating the components alone.

Example 3

A solvent-treated coastal neutral distillate having the following properties:

Sayb. visc. at 100° F.	530
Sayb. visc. at 210° F.	59
Sp. gr. 60° F./60° F.	.8996
ASTM pour point	−20
Refr. index at 20° C.	1.4928

was initially acid-treated with 10% of its weight of 66° Bé. sulfuric acid. Thereafter the sample was treated with three equal dumps of oleum calculated as 104.5% H_2SO_4, the dumps being 10% by weight of the distillate in each case. The reaction mixture was allowed to settle overnight after each successive acid dump and in each case separated from the acid sludge. The acid-treated oil was worked up in a manner analogous to that described in Example 2 and a crude petroleum mahogany soap containing sodium sulfonate (calculated dry) equivalent to a yield of 6.4% by weight of the neutral distillate employed was obtained. The average molecular weight of this dry sodium sulfonate was 505.

The coastal neutral distillate remaining after extraction with aqueous alcohol after having been treated with the single 10% by weight dump of 66° Bé. sulfuric acid and one 10% by weight dump of the oleum calculated as 104.5% H_2SO_4 was, at this point, blended with the dodecylbenzene still bottoms sample described in Example 1, using 52.4% by weight of acid-treated neutral distillate to 47.6% by weight of dodecylbenzene still bottoms. This blend was treated with a total of 70% by weight of oleum calculated as 104.5% H_2SO_4 in four equal dumps in the manner described in Example 1. The resulting mixture of sulfonic acids had a Saybolt viscosity at 100° F. of 3,583.

The yield of sodium sulfonate (calculated dry) obtained in the manner set forth in Example 1 had an average molecular weight of 451 and comprised 45.9% by weight of the starting blend of dodecylbenzene still bottoms and acid-treated neutral distillate. Since 38.7% of the yield would normally be obtained from the dodecylbenzene still bottoms (as shown by multiplying 47.6% × 81.3) and 3.35% of the yield would normally be obtained from the acid-treated neutral distillate employed, the total calculated yield is 42.05%. Since the actual yield of sodium sulfonate (calculated dry) is 45.9%, the total sulfonate yield from the blend is 3.85% by weight higher than the yield obtained by separately sulfonating the components.

Example 4

A petroleum oil having the following physical properties:

Sayb. visc. at 100° F	117
Sp. gr. 60° F./60° F	.8724
ASTM pour point	−5
Refr. index at 20° C	1.4793

was acid-treated with two dumps totalling 15% by weight of oleum calculated as 104.5% H_2SO_4 in a manner similar to that described in Example 3. This acid-treated oil was then blended with the dodecylbenzene still bottom sample described in Example 1, using 44.1% by weight of acid-treated oil to 55.9% by weight of dodecylbenzene still bottoms. The blend was thereupon treated with a total of 65% by weight of oleum calculated as 104.5% H_2SO_4 in four equal dumps in the manner described in Example 3. The reaction mixture of sulfonic acids had a Saybolt viscosity at 100° F. of 1,663, and the yield of sodium sulfonate (calculated dry) was, as in Examples 2 and 3, higher than the yield obtained by sulfonating the individual components separately.

As is seen from the foregoing examples, where a petroleum lubricating oil fraction was employed in conjunction with a sample of dodecylbenzene still bottoms and the mixture thereof sulfonated, the resulting viscosity of the reaction mixture was considerably lower than that which should have been normally expected by way of the aggregate viscosities of the otherwise identically but separately sulfonated components. This lowering of the viscosity is surprising in its extent, in that the viscosity of the sulfonated reaction mix is a mere fraction of what is ordinarily expected, and further, is lower than could be obtained by a mere dilution of the sulfonated still bottoms with a corresponding amount of diluent. Thus, a synergistic effect with respect to the presence of the petroleum lubricating oil fraction is decidedly present. In addition, in all examples, the final sulfonates produced showed no turbidity or cloudiness whatever upon long standing. It is further apparent from the examples that the final yield of petroleum mahogany sulfonate obtained with the presence in the reaction mix of the petroleum lubricating oil fraction, as compared with that obtained in the absence of such fraction, is higher than the aggregate yields which could be expected from the individual yields of the separately sulfonated components.

We claim:

1. In the production of oil-soluble sulfonates from dodecylbenzene still bottoms having an average molecular weight above 300, the improvement which comprises blending said still bottoms with a petroleum lubricating oil fraction having a Saybolt viscosity at 100° F. of from 30–700 seconds, thereby producing a blend, thereafter sulfonating the blend, thereby producing sulfonic acids, neutralizing the said sulfonic acids, thereby producing sulfonates, and recovering the sulfonates so produced.

2. Process according to claim 1 in which the said blend contains from 20–60% of said petroleum lubricating oil fraction.

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