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PURIFICATION OF ALKYL ARYL SULFONATES

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The present invention relates to the production of neutral alkyl aryl sulfonates and relates more particularly to the production of neutralized alkyl aryl sulfonates which are substantially free of color bodies.

Sulfonation of alkyl aryl hydrocarbons has generally followed the procedure wherein about 1.3 to 2 parts by weight of 100 to 105 percent sulfuric acid is used per part by weight of the alkyl aryl hydrocarbon. Other sulfonating agents have been used but whatever agent was used the resulting mixture upon completion of the sulfonation reaction produced an off-colored sulfonate upon neutralization with a base such as sodum hydroxide. Since such colored sulfonates can only be used in a relatively few applications, various methods have been suggested for removing the color bodies. Light colored sulfonates are particularly desirable in a laundry detergent. Methods as used heretofore have involved treating aqueous solutions of metal sulfonates with hydrogen peroxide or other bleaching agent such as alkali peroxide. Other treating agents have included solutions of a metal persalt such as an alkali metal perborate, or an alkali metal persulfate. In addition, aqueous sulfonates have been blown with oxygen or oxidizing gas in order to improve the color of the product. None of these methods have been entirely satisfactory, generally because they have involved an undesirable expenditure of materials and time and furthermore the product so obtained has not been improved greatly in color.

It is, therefore, a principal object of the present invention to provide an improved process which obviates the disadvantages of the prior art processes. It is another object of our invention to provide an improved method for the treatment of alkyl aryl sulfonic acids whereby substantially colorless sulfonates may be obtained upon neutralizing the treated sulfonic acid. Other objects and advantages of the invention will become 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 principle of the invention may be employed.

The foregoing objects and advantages are attained by a process which in brief involves the following steps: An alkyl aryl hydrocarbon is reacted with a sulfonating agent such as sulfuric acid, oleum or sulfur trioxide. Following sulfonation, the spent sulfonating agent is removed from the mixture comprising the sulfonic acid and the spent sulfonating agent. The recovered sulfonic acid is then bleached by treating it with hydrogen peroxide in the presence of a water soluble organic base. Finally after treatment with the hydrogen peroxide, the sulfonic acid is neutralized.

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

Suitable alkyl aryl hydrocarbons which may be used are those obtained by the reaction of excess benzene, toluene, xylene, naphthalene or similar hydrocarbons with

an alkylating agent in the presence of a Friedel-Crafts type catalyst such as boron fluoride, hydrogen fluoride, sulfuric acid, etc. The alkylating agent may be a 9 to 18 carbon straight or branched chain olefin, alcohol or halide. A suitable straight or branched chain olefin is produced from a tetradecane fraction having a boiling range of 240–260° C. which is obtained by fractionating kerosene. Branched chain olefins are preferred, however, as the alkylating agent, such as the 9 to 18 carbon polymers of propylene including trimers, tetramers, pentamers, or mixtures thereof. Other alkylating agents that may be used include the branched chain nonyl, decyl, dodecyl, octadecyl alcohols and chlorides.

A suitable alkyl aryl hydrocarbon which is also available commercially in large quantities is a blend of monoalkylbenzenes sometimes called dodecylbenzene. This particular product is obtainable from Continental Oil Company under the trade name "Neolene 400." Typical physical properties of dodecylbenzene or "Neolene 400" are as follows:

Specific gravity at 16° C	0.8742
Average molecular weight	232
A.S.T.M., .D–158 Engler distillation:	
I.B.P. ° F.	535
5 ° F.	545
10 ° F.	550
50 ° F.	560
90 ° F.	580
97 ° F.	592
F.B.P. ° F.	603
Refractive index at 20° C	1.4885
Viscosity at 20° C., cp	14
Bromine number	0.16

The sulfonating of the alkyl aryl hydrocarbons may be carried out by methods well known to those skilled in the art using sulfuric acid or oleum as the sulfonating agent. Other suitable sulfonating agents which may be used include chlorosulfonic acid, sulfur trioxide, etc. If desired the alkyl aryl hydrocarbon may be diluted with a solvent such as a mineral oil, halogenated hydrocarbon, or sulfur dioxide prior to sulfonation. Sulfur trioxide is the preferred sulfonating agent as the use of this compound makes it possible to prepare neutralized sulfonate compositions containing a minimum of inorganic salts. When sulfur trioxide is employed there is a tendency to form sulfonic acid anhydrides and perhaps other similar products which cause the phenomenon known as "pH reversion" or "acid drift."

This phenomenon "pH reversion" is discussed further in the co-pending application of James C. Kirk and Edsel L. Miller entitled "Preparation of Stable Alkaryl Sulfonates," Serial No. 480,068, filed January 5, 1955, now Patent No. 2,928,867 together with means by which this reversion can be prevented. The foregoing co-pending application is assigned to the same assignee to which our invention is assigned and the disclosure of the co-pending application is hereby made a part of our application.

The bleaching agent employed is hydrogen peroxide and suitable quantities of this compound vary from about 0.1 to 3 weight percent of 100 percent hydrogen peroxide based on the weight of the sulfonic acid. Although hydrogen peroxide solutions ranging from about 3 to 100 percent may be used, we prefer to use a solution having a concentration of about 30%. As to the temperature during the bleaching process, that may range from about 20 to 75° C., however, we prefer to employ a temperature within a range of about 20 to 25° C. The procedure of bleaching sulfonic acid compositions using hydrogen peroxide is discussed in U.S. Patent 2,806,055 entitled "Purification of Alkaryl Sulfonates" issued to George C.

Feighner September 10, 1957. The disclosure contained therein is hereby made a part of the present application.

Suitable organic bases include water soluble amines and urea. Specific water soluble amines which we have found to be highly desirable for use in our process are triethanolamine and isopropylamine. As to the amount of the organic base added that may vary from about 1 to 4 weight percent based on the weight of the sulfonic acid. A larger quantity of the organic base, of course, may be used without any detrimental effects. These organic bases are relatively expensive and for that reason we generally try to use the minimum amount of the organic base which will still give good results and for that reason we prefer to use an amount that varies from about 1 to 2 weight percent based on the weight of the sulfonic acid.

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 that the invention is not to be limited to the specific conditions or details set forth in these examples except insofar as such limitations are specified in the appended claims. Parts given are parts by weight.

EXAMPLE 1

In this example and the succeeding examples the dodecylbenzene sulfonic acid used was prepared by sulfonating dodecylbenzene using sulfur trioxide as the sulfonating agent following the procedure of Example 2 of U.S. Patent 2,806,055. Two samples of dodecylbenzene sulfonic acid were prepared. Immediately after preparing the acid 1 part of water was added to 100 parts of the acid to hydrolyze the anhydrides. Each sample was divided into two equal portions, to one portion was added 2 parts of triethanolamine per 100 parts of the acid two hours after the addition of the water. All four samples were stored at room temperature for 42 days. At the end of this storage period, the acid was neutralized by adding thereto sodium hydroxide. For comparison purposes a sample of each acid was neutralized prior to the storage period, the salt added to water and the color determined as a control. In all cases the amount of the salt added to the water was such that the concentrations of the sodium sulfonate in water was the same. The experiments together with the results are summarized in Table 1 below.

Table 1

Sample	Color	
	Acid No. 1	Acid No. 2
Control	0.50 RCD	0.58 RCD
42 days' storage no additive used	0.59 RCD	0.70 RCD
42 days' storage 2 parts triethanolamine added	0.49 RCD	0.55 RCD

RCD is an abbreviation of relative color density and is determined by a method which can be described as follows:

OUTLINE OF METHOD

The colorimeter reading obtained on an aqueous solution of slurry containing 4 percent active ingredient is compared to that obtained on a standard chromate solution. The ratio of the two readings is reported as the relative color density (RCD) of the sample.

APPARATUS

Klett-Summerson photoelectric colorimeter
Cell, 4 cm., rectangular
Color filter, Klett No. 42

REAGENTS

Standard chromate solution, containing 2 mg. $K_2Cr_2O_7$ per 100 ml. 0.05 N KCH. Prepare a stock solution of potassium dichromate by dissolving 0.200 g. reagent grade $K_2Cr_2O_7$ in water and diluting to 100 ml. in a volumetric flask. Dissolve 3.2 to 3.3 g. of reagent grade potassium hydroxide (85 to 86 percent KOH) in approximately 500 ml. of water contained in a one-liter volumetric flask. Add by pipette 10 ml. of the stock dichromate solution, cool at room temperature, dilute to one liter, and mix well. Store in a glass-stoppered bottle.

PROCEDURE

Calculate the weight of sample needed to give 100 ml. of an aqueous solution containing 4 percent active ingredient. For example, a C–50 slurry with 40 percent active calculates 10 g. of slurry per 100 ml. of solution. Weigh (with a precision of 1 percent of sample weight) the calculated amount of slurry into a 100-ml. beaker. Add 25 to 30 ml. of water to the beaker and heat gently on a low temperature hot plate, with stirring, until the slurry is dissolved. Cool and quantitatively transfer the solution into a 100-ml. volumetric flask. Dilute to 100 ml. and mix thoroughly.

Place the No. 42 color filter in the Klett, set the slide for use with rectangular cells, and turn on the light switch. Let the colorimeter "warm up" for 10 to 15 minutes. Fill a 4 cm. rectangular cell with distilled water, place the cell in the instrument, and adjust to zero reading. Discard the water in the cell. Rinse the cell with two small portions of the sample solution, fill, place the cell in the instrument, and obtain the reading. Discard the solution and rinse the cell with water, then twice with the standard chromate solution. Fill the cell, place in the instrument, and obtain the reading. Discard the standard solution and rinse the cell with water and dry.

CALCULATION

Calculate the relative color density of the sample solution as follows:

$$\text{Relative color density (RCD)} = \frac{\text{Reading of sample solution}}{\text{Reading of standard solution}}$$

EXAMPLE 2

In this example dodecylbenzene sulfonic acid was bleached using 1.5 parts of 30% hydrogen peroxide per 100 parts of acid for a period of 20 minutes. The bleached acid was divided into twelve equal portions, the organic bases in the amounts specified added, and the acid samples stored for a period of 72 hours at 110° F. after which the colors of the acid samples were compared visually. The results are summarized in Table 2 below.

Table 2

Organic base	Parts of base added per 100 parts of acid			
	1.0	2.0	3.0	4.0
Triethanolamine				x
Isopropylamine		x		
Urea	x			

x—Denotes color of about equal intensity.

EXAMPLE 3

In this example the dodecylbenzene sulfonic acid was divided into four equal portions and the components listed below added immediately.

Sample No.:	Additive
1	1% water 2% triethanolamine.
2	1% water 1% urea.
3	1% water 2% urea.
4	1% water.

The acid samples were neutralized and the color of the sulfonate slurries determined. Samples 1, 2, and 3 were stored in an oven at 110° F. for a period of time varying

from 66 to 330 hours. The results are summarized below.

Table 3

Sample No.	RCD color of sodium sulfonate slurry			
	0 hrs.	66 hrs.	138 hrs.	330 hrs.
1	0.64	0.80	0.80	0.91
2	0.38	0.52	0.51	0.64
3	0.45	0.57	0.52	0.71
4	0.98			

EXAMPLE 4

In this example the dodecylbenzene sulfonic acid was divided into a plurality of portions the organic base added in parts per 100 parts of acid and then the acid was bleached using varying amounts of hydrogen peroxide after which the different portions were stored for varying periods of time at 110° F. The results are summarized below.

[Color in RCD]

Hours at 110° F.	2 parts triethanolamine, percent bleach				2 parts urea, percent bleach				1 part urea, percent bleach			
	0.1	0.2	0.35	0.5	0.1	0.2	0.35	0.5	0.1	0.2	0.35	0.5
0	.50	.42	.26	.19	.41	.31	.23	.20	.37	.39	.23	.20
66	.57	.48	.47	.47	.45	.46	.43	.43	.43	.51	.44	.49
138	.53	.49	.43	.46	.48	.46	.46	.53	.43	.42	.51	.53
330	.68	.61	.62	.62	.57	.55	.57	.59	.63	.54	.56	.62

EXAMPLE 5

Since for practical purposes a 0.35 bleach generally gave the best results, sulfonic acid samples were bleached before and after aging with the results summarized below.

Table 5

[Color in RCD]

Hrs at 110° F.	2 parts triethanolamine, 0.35% bleach		2 parts urea, 0.35% bleach		1 part urea, 0.35% bleach	
	Bleached before aging	Bleached after aging	Bleached before aging	Bleached after aging	Bleached before aging	Bleached after aging
0	.26	.26	.23	.23	.23	.23
66	.47	.27	.43	.25	.44	.27
138	.48	.28	.46	.23	.51	.24
330	.62	.44	.57	.31	.56	.35

The data reported above show that the organic base may be added with the water prior to bleaching if desired. In fact, in many cases that is the preferred procedure. These data also show that it is much better to bleach the acid just prior to use rather than bleach immediately after preparing the acid and then storing it until it is used.

Although the examples given above are specific to dodecylbenzene sulfonic acid our invention is not so limited but can be used for the improvement in color of other sulfonic acids. As an additional example the product known as dodecylbenzene intermediate sulfonic acid is improved in color by the procedure of this invention. Dodecylbenzene intermediate sulfonic acid is obtained by sulfonating the hydrocarbon known as dodecylbenzene intermediate. Its typical physical properties are as follows:

Gravity, API	40.4
Average molecular weight	193
Percent sulfonatable	57
A.S.T.M., .D–158 Engler distillation:	
I.B.P. °F	353
5 °F	371
50 °F	393
90 °F	433
95 °F	448
F.B.P. °F	488
Refractive index at 25° C	1.4688
Viscosity at 100° F centipoises	1.33
Aniline point °F	82

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.

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

1. In a method for the preparation of alkyl aryl sulfonic acids of improved color comprising (1) reacting an alkyl aryl hydrocarbon wherein said aryl radical is selected from the group consisting of phenyl, tolyl and xylyl radicals, and said alkyl radicals contain from 9–18 carbon atoms therein with a sulfonating agent selected from the group consisting of chlorosulfonic acid, sulfur trioxide, sulfuric acid and oleum, (2) separating spent sulfonating agent, (3) hydrolyzing any sulfonic acid anhydrides present with water, (4) bleaching said sulfonic acid by treatment with 0.1 to 3 weight percent of hydrogen peroxide, the improvement consisting of adding 1–4 weight percent of a water soluble organic nitrogen base selected from the group consisting of triethanolamine, isopropylamine and urea subsequent to the hydrolysis of any sulfonic acid anhydrides and prior to said bleaching.

2. A process according to claim 1 wherein the alkyl aryl hydrocarbon is dodecylbenzene and the sulfonating agent is sulfur trioxide.

3. In a method for the preparation of alkyl aryl sulfonates of improved color comprising (1) reacting an alkyl aryl hydrocarbon wherein said aryl radical is selected from the group consisting of phenyl, tolyl and xylyl radicals, and said alkyl radicals contain from 9–18 carbon atoms therein with a sulfonating agent selected from the group consisting of chloro-sulfonic acid, sulfur trioxide, sulfuric acid and oleum, (2) separating spent sulfonating agent, (3) hydrolyzing any sulfonic acid anhydrides present with water, (4) bleaching said sulfonic acid by treatment with 0.1–3 weight percent of hydrogen peroxide, and (5) neutralizing said bleached sulfonic acid, the improvement consisting of adding 1–4 weight percent of a water soluble organic nitrogen base selected from the group consisting of triethanolamine, isopropylamine and urea subsequent to the hydrolysis of any sulfonic acid anhydrides and prior to said bleaching.

4. A method according to claim 3 wherein the alkyl aryl hydrocarbon is dodecylbenzene and the sulfonating agent is sulfur trioxide.

References Cited in the file of this patent

UNITED STATES PATENTS

2,805,249	Gilbert et al.	Sept. 3, 1957
2,806,055	Feighner	Sept. 10, 1957
2,827,484	Carlson et al.	Mar. 18, 1958

FOREIGN PATENTS

88,982	Netherlands	Aug. 15, 1958