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COLOR STABILIZATION OF ALKYLARENESULFONIC ACIDS

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This invention relates to a process for producing improved sulfonic acid compositions. More particularly, the invention relates to a method for improving the color and color stability of alkylarenesulfonic acids. A preferred embodiment of the invention relates especially to such sulfonic acids obtained by sulfonation with liquid H_2SO_4 or oleum.

Alkylarenesulfonate salts, and particularly long-chain alkylbenzenesulfonate salts, are outstanding surface-active agents for use in synthetic detergent formulations, especially those adapted for use as household detergents. Principally because of aesthetic considerations it has recently become of considerable commercial importance that alkylarenesulfonate salts should be as white as possible. Unfortunately, however, the whiteness of alkylarenesulfonate salts is limited by the color of the sulfonic acids from which the salts are prepared—and it is extremely difficult to obtain the sulfonic acids free of darkly discoloring impurities.

In a copending application Serial No. 611,352, filed September 21, 1956, it has been disclosed that the color of alkylarenesulfonic acids can be markedly improved by a bleaching process utilizing hydrogen peroxide. As is indicated in that application, the improved sulfonic acids produced by the bleaching process are not completely color stable—and consequently must be converted to sulfonate salts soon after bleaching. If this were not done, the sulfonic acids would soon (within a matter of a day or so) begin to redevelop the undesirable dark discoloration.

The color instability of hydrogen peroxide bleached sulfonic acids is particularly prevalent and noticeable in alkylarenesulfonic acids produced by sulfonation with liquid sulfuric acid and/or oleum. Consequently, a preferred embodiment of this invention is particularly concerned with such sulfonic acids. (Sulfonations with H_2SO_4 and with oleum are considered interchangeable for purposes of the present invention, and both are included in the term "sulfuric acid sulfonation.") These latter sulfonic acids generally contain free sulfuric acid dissolved or dispersed therein in considerably higher proportions (e.g., more than about 3 wt. percent and as much as 15 or 20 wt. percent or more) than the sulfonic acids prepared by SO_3 sulfonation.

We have now found that the color stability after bleaching the aforementioned alkylarenesulfonic acids can be very much improved by treating such sulfonic acids with alkaline neutralizing agents in minor amounts, and preferably in an amount approximately sufficient to convert (on a stoichiometric basis) the free sulfuric acid in said composition to a bisulfate salt.

The practice of the present invention, as well as the remarkable benefits obtained therefrom, are illustrated in the following example.

EXAMPLE

A sample of crude dodecylbenzenesulfonic acid was prepared by sulfonating dodecylbenzene (from benzene alkylation with propylene tetramer) with 100% H_2SO_4. The crude dodecylbenezenesulfonic acid had the following analysis:

	Percent
Dodecylbenzenesulfonic acid	85.10
Sulfuric acid (as 100%)	6.75
Unsulfonated oil	2.70
Water	5.45

Fifty parts by weight of the crude dodecylbenzenesulfonic acid was diluted with 5 parts by weight of water (in order to reduce the viscosity of the crude acid). Then, while holding the temperature between about 45° and 50° C., 1 part by weight of 30% aqueous hydrogen peroxide solution was added with mild agitation. The clarity of the resulting bleached composition was evaluated by determining the percent transmission (relative to distilled water) of light through a 4% aqueous solution. The determinations were made in a 50 millimeter rectangular cell utilizing a Fisher electrophotometer equipped with a 425 millimicron blue filter. The light transmission of the bleached acid was measured immediately after bleaching and at specified subsequent periods during storage at 25°–26° C. The results are tabulated in the table below.

A second sample of the crude dodecylbenzenesulfonic acid was bleached in the same manner as described above. Immediately after bleaching, 3.8 parts by weight of a 50% aqueous sodium hydroxide solution was added to the acid at a temperature between 45° and 50° C. The light transmission was then determined as with the preceding sample.

Table

Treatment	Relative Transmission					
	First Day, Percent	After 5 Days, Percent	After 12 Days, Percent	After 24 Days, Percent	After 55 Days, Percent	After 82 Days, Percent
H_2O_2	73	74	58	45	28	19
H_2O_2+NaOH	88	89	91	89	91	81

From the foregoing results it is readily seen that sulfonic acid compositions bleached and treated according to the present invention are very markedly stabilized against color degradation.

It will be readily aparent to those skilled in the art that the procedure described in the preceding example is subject to considerable variation without departing from the basic invention disclosed herein. For example, in the procedure described above the crude acids were first treated with hydrogen peroxide and then treated with an alkaline neutralizing agent. However, if desired or convenient this order of treatment can be reversed; or the two treatments can be carried out simultaneously. In the case of simultaneous treatment with hydrogen peroxide and alkaline neutralizing agent, particular care should be exercised in effecting sufficiently rapid removal of heat to maintain the reaction tempera-

ture below about 50 or 55° C. If the temperature is allowed to rise above 50 or 55° C. for more than a short time, there is a tendency toward degradation and undesirable discoloration of the product.

It will be readily apparent that the present invention is applicable to a wide variety of alkylarenesulfonic acids. In general, it is applicable to long-chain alkyl substituted arenesulfonic acids such as those having between about 9 and about 22 carbon atoms in the alkyl groups. The process is applicable to arenesulfonic acids containing a plurality of alkyl groups, but treatment of monoalkylarenesulfonic acids is preferred. Since the problems of discoloration are greater with alkylarenesulfonic acids in which the alkyl groups are branched (for example, alkylarenesulfonic acids in which the alkyl group is derived from polypropylene or polybutylene) the present invention is particularly useful in the treatment of branched-chain monoalkylarenesulfonic acids.

The amount of hydrogen peroxide to be utilized in bleaching the crude sulfonic acid compositions will depend to a considerable extent upon the degree of discoloration of the crude acid, the desired degree of bleaching, the times and temperatures utilized in the bleaching step of the process, the efficiency with which the hydrogen peroxide is dispersed within the crude acid, the form in which the hydrogen peroxide utilized (for example, concentration of aqueous solution), etc. In general, however, the amount of hydrogen peroxide to be used will fall between about 0.1 wt. percent and about 3 wt. percent, and preferably between about 0.5 wt. percent and about 2 wt. percent, based upon the weight of crude alkylarenesulfonic acid.

Since one of the principal purposes of treating with an alkaline neutralizing agent is to at least partially neutralize a substantial portion of the free sulfuric acid (though without neutralizing an appreciable proportion of the sulfonic acid) it will be readily recognized that a wide variety of alkaline neutralizing agents can be used in place of the sodium hydroxide of the foregoing example. In general, alkaline materials such as the alkali and alkaline earth metal hydroxides and carbonates (and particularly sodium, potassium or calcium hydroxides or carbonates) will be the most practical neutralizing agents. However, ammonia, ammonium hydroxide, ammonium carbonate, and various organic amines such as mono, di, or triethanolamine, mono or dimethylamine, mono or diethylamine, cyclohexylamine or dicyclohexylamine, etc. can be used if desired.

The amount of alkaline neutralizing agent used in the example described above was approximately sufficient to convert (on stoichiometric basis) the free sulfuric acid to bisulfate ion. This concentration can be varied somewhat while still obtaining an appreciable degree of color stability. For example, concentrations running as low as 40% (of the stoichiometric amount necessary to convert H_2SO_4 to HSO_4^-) will still give noticeable stabilization. The upper limit of concentration is considerably more critical—about 120% being the upper operable limit for carrying out the process.

Some degree of care must be exercised with respect to the amount of water which is allowed in the sulfonic acid compositions during treatment according to this invention. All crude compositions will contain at least a small amount of water therein. As indicated above, further amounts of water may be added to reduce the viscosity of the crude acid and facilitate further handling and treatment thereof. Moreover, since hydrogen peroxide and most alkaline neutralizing agents are more readily handled as aqueous solutions, further quantities of water will often be introduced with these latter treating agents. If the total amount of water from all of these sources approaches the neighborhood of 30 wt. percent of the sulfonic acid compositions, there is a strong tendency toward the formation of gel structures which make further handling and treatment very difficult. Consequently, it is preferred that the total water concentration be kept below about 25 wt. percent. When the ultimate sulfonic acid composition is to be utilized in a so-called "dry neutralization" for the direct production of a dry free-flowing detergent composition (as described in more detail in the earlier application Serial No. 611,352), it is preferred that the total water content be kept below about 10 wt. percent.

What is claimed is:

1. A process for producing a clear color-stabilized alkylarenesulfonic acid containing from about 9 to about 22 carbon atoms in the alkyl groups thereof, said stabilized alkylarenesulfonic acid being prepared from a crude alkylarenesulfonic acid having dispersed therein an appreciable proportion of sulfuric acid, which process comprises treating said crude sulfonic acid with (1) hydrogen peroxide in a minor amount up to about 3 wt. percent and (2) an alkaline neutralizing agent in a minor amount stoichiometrically sufficient to convert a predominant proportion of the sulfuric acid to bissulfate salt without neutralizing a substantial proportion of the sulfonic acid.

2. A process for producing a clear color-stabilized branched-chain alkylarenesulfonic acid containing from about 9 to about 22 carbon atoms in the branched-chain alkyl group thereof, said stabilized sulfonic acid being prepared from a crude branched-chain alkylarenesulfonic acid produced by liquid phase sulfuric acid sulfonation and containing dispersed therein an appreciable proportion greater than 1 wt. percent of sulfuric acid, which process comprises treating said crude sulfonic acid with (1) hydrogen peroxide in a minor amount up to about 3 wt. percent and (2) an alkaline neutralizing agent in a minor amount up to about 1.2 times that stoichiometrically sufficient to convert the aforesaid sulfuric acid to a bisulfate salt.

3. A process for producing a clear color-stabilized branched-chain monoalkylarenesulfonic acid containing from about 9 to about 22 carbon atoms in the alkyl group thereof, said stabilized sulfonic acid being prepared from a crude branched-chain monoalkylarenesulfonic acid produced by liquid phase sulfuric acid sulfonation and containing dispersed therein an appreciable proportion greater than 1 wt. percent of sulfuric acid, which process comprises treating said crude sulfonic acid with (1) hydrogen peroxide in a minor amount up to about 3 wt. percent and (2) an alkaline neutralizing agent selected from the group consisting of alkali and alkaline earth metal hydroxides and carbonates in a minor amount up to about 1.2 times that stoichiometrically sufficient to convert the aforesaid sulfuric acid to a bisulfate salt.

4. A process for producing a clear color-stabilized branched-chain monoalkylarenesulfonic acid containing from about 9 to 22 carbon atoms in the alkyl group thereof, said stabilized sulfonic acid being prepared from a crude branched-chain monoalkylarenesulfonic acid produced by liquid phase sulfuric acid sulfonation and containing dispersed therein between about 1 and about 10 wt. percent of sulfuric acid, which process comprises treating said crude sulfonic acid with (1) hydrogen peroxide in a minor amount up to about 3 wt. percent and (2) an alkaline neutralizing agent selected from the group consisting of alkali metal and alkaline earth metal hydroxides and carbonates in a minor amount between about 40% and about 120% of that stoichiometrically required to convert the aforesaid sulfuric acid to a bisulfate salt.

5. A process for producing a clear color-stabilized branched-chain dodecylbenzenesulfonic acid, said stabilized sulfonic acid being prepared from a crude branched-chain dodecylbenzenesulfonic acid produced by liquid phase sulfuric acid sulfonation and containing dispersed therein between about 1 and about 10 wt. percent of sufuric acid, which process comprises treating said crude

sulfonic acid with (1) hydrogen peroxide in a minor amount between about 0.5 and about 2 wt. percent and (2) sodium hydroxide in an amount approximately stoichiometrically sufficient to convert the aforesaid sulfuric acid to a bisulfate salt.

6. A process for producing a clear color-stabilized branched-chain tridecylbenzenesulfonic acid, said stabilized sulfonic acid being prepared from a crude branched-chain tridecylbenzenesulfonic acid produced by liquid phase sulfuric acid sulfonation and containing dispersed therein between about 1 and about 10 wt. percent of

sulfuric acid, which process comprises treating said crude sulfonic acid with (1) hydrogen peroxide in a minor amount between about 0.5 and about 2 wt. percent and (2) sodium hydroxide in an amount approximately stoichiometrically sufficient to convert the aforesaid sulfuric acid to a bisulfate salt.

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