METHOD OF BLEACHING ALKYL ARLY SULFONIC ACIDS

Leo J. Weaver, Wakefield, Mass., assignor to Monsanto Chemical Company, St. Louis, Mo., a corporation of Delaware

No Drawing. Application September 21, 1956

Serial No. 611,352

11 Claims. (Cl. 252—138)

The present invention relates to a controlled process of effecting hydrogen peroxide bleaching of alkyl aryl sulfonic acid compositions which are suitable as the active component in detergent formulations. More specifically this invention relates to the process of controlled bleaching of a monoalkylbenzene sulfonic acid with hydrogen peroxide.

The principal object of this invention is to produce an alkyl aryl sulfonic acid having a materially improved color. Another object of this invention is to retain the benifit of the low-color, bleached sulfonic acid by stabilization, including neutralization thereof, to provide an alkyl aryl sulfonate which is substantially white. Still another object of this invention is to effect "dry" neutralization of the bleached alkyl aryl sulfonic acid with solid, pulverulent, anhydrous, alkali metal salts with or without the presence of detergent builder salts, to directly produce a high-active detergent composition. Further objects and advantages of this invention will be apparent from the following description and appended claims.

It is well known that hydrogen peroxide is relatively stable in the presence of acids and in fact acids, such as phosphoric acid, are employed as stabilizers therein. Accordingly, it has not been considered possible to effect satisfactory direct bleaching of sulfonic acids with hydrogen peroxide.

The alkylbenzene sulfonic acids are black opaque materials as they come from the sulfonation process. Herefore various alkaline metal hypochlorites, particularly sodium hypochlorite, have been employed to bleach alkyl aryl sulfonates, but it has been found that the excessive use of hypochlorite bleaches depress the foam stability of the alkylbenzene sulfonate. Also the use of hypochlorite bleaches introduces the chloride ion to the detergent active composition and will normally be present as sodium chloride therein, the presence of which may be deleterious for certain applications.

The olefin-monoalkylbenzene sulfonic acids are prepared by procedures well known to the art. For example benzene can be alkylated with a polypropylene in the presence of a Friedel-Crafts catalyst and there after the alkylated benzene can be sulfonated with sulfuric acid, oleum, or sulfur trioxide in any suitable manner. The alkyl groups in the aforesaid sulfonic acids for the instant process contain from about 9 to about 22 carbon atoms, preferably from about 9 to about 18 carbon atoms, and more preferably still contain an average of about 12 carbon atoms, such as those obtained by alkylation of benzene with decene-1, dodecene-1, pentadecene-1, octadecene-1, tetrapropylene, hexapropylene, pentabutylene, and other olefin polymers, e. g. propylene polymers, and the like.

Dodecylbenzene sulfonic acid and mixtures of alkylbenzene sulfonic acids containing a substantial quantity of dodecylbenzene sulfonic acid or closely related al-
but preferably only about 5 to about 10 percent of water is needed. It is to be noted that the minimum amount of water necessary for addition to the sulfonic acid will vary somewhat according to the process employed to produce the sulfonic acid, for example whether sulfonation was effected with sulfuric acid, oleum or sulfur trioxide. This will be more clearly understood by reference to a specific example as in the preparation of dodecylbenzene sulfonic acid wherein the typical commercial product prepared by the 100 percent sulfuric acid sulfonation process generally contains about 88 percent dodecylbenzene sulfonic acid, 8 percent sulfuric acid, 3 percent water, and 1 percent unsulfonated oils, since a portion of the reactant acid is soluble in the sulfonic acid, and the material prepared by sulfur trioxide sulfonation is substantially free from water. Accordingly, the instant bleaching process as applied to dodecylbenzene sulfonic acid prepared by sulfur trioxide sulfonation will normally require the addition of a larger amount of water than will the material prepared with 100 percent sulfuric acid. The instant process can also be employed, for example, directly with the sulfonation reaction mixture prior to the separation of any spent acid, i.e. a mixture of about 50 weight percent of sulfuric acid and 50 weight percent of the sulfonic acid, after adding sufficient water to provide a spent acid concentrate of at least about 80 percent. This modification requires a larger amount of hydrogen peroxide since the spent acid is also bleached to a substantially water-white color and the sulfonic acid can be separated and utilized, per se, or fortified with oleum or sulfur trioxide to provide a higher-strength acid.

Hydrogen peroxide is commercially available in a number of grades as solutions containing varying amounts of hydrogen peroxide such as 3%, 6%, 27.5%, 30%, 35%, 50%, 90%, and 99.4%. The high-strength materials are too active for direct addition to the sulfonic acid since they cause degradation of the acid. Whereas the dilute solutions can be employed the additional water introduced therein may limit the use of the bleached sulfonic acid in the "dry" neutralization process for the preparation of detergent compositions. The preferred concentration of hydrogen peroxide is 30%, but equivalent amounts of medium-strength solutions can be employed. The quantity of 30% hydrogen peroxide necessary to effectively bleach the sulfonic acid may range up to about 5 percent by weight of the acid, but preferably ranges from about 1 to about 3 percent thereof. It is desirable to avoid the use of excess hydrogen peroxide since its presence may ultimately cause degradation of the alkylbenzene sulfonic acid if it is subject to relatively high temperature during storage and transit. If the maximum temperature to which the bleached sulfonic acid is subjected does not exceed about 25 to 30°C, the reaction does not present any serious problem. When the storage and transit temperatures are in doubt it is desirable to treat the bleached sulfonic acid with from about 1 to about 2 percent by volume of a saturated solution of sodium bisulfite to stabilize the treated acid. Also the use of excess hydrogen peroxide imparts a fruity ester-type odor to the sulfonic acid which is undesirable in detergent compositions produced therefrom.

The hydrogen peroxide solution is slowly added while maintaining sufficient agitation to preclude local overheating and degradation of the sulfonic acid as hereinabove pointed out. The process is designed to provide a sojourn time of at least about 15 minutes to one-half hour at 40°C to 55°C and can be aged thereafter at room temperature for about 12-24 hours or more prior to stabilization. In order to be assured of maximum freedom from color in the final detergent composition the sulfonic acid should be bleached while it is still relatively fresh and preferably should be neutralized soon after the bleaching operation is completed. The sulfonic acid can be directly neutralized with an alkali metal hydroxide such as sodium hydroxide, potassium hydroxide, and the like, to provide a paste or slurry of an extremely white detergent active composition or a pulverulent anhydrous alkali metal salt can be employed, such as sodium carbonate, sodium bicarbonate, sodium tripolyphosphate, tetrasodium pyrophosphate, sodium metasilicate, potassium tripolyphosphate, tetrapotassium pyrophosphate, and the like, to effect a "dry" neutralization and direct production of a dry, free-flowing detergent composition which is characterized by a materially improved degree of whiteness. The "dry" neutralization is preferably effected by spraying the bleached sulfonic acid onto the agitated, finely divided, anhydrous alkali metal salts and thereafter spraying a small amount of water onto the agitated substantially uniform mixture of the sulfonic acid and the alkali metal salt, but in an amount not to exceed a total water content present in the final composition which is equivalent to the quantity of water which can be held in the form of the hydrates of the alkali metal salt.

The bleached sulfonic acid and water can also be added by other means, as pouring in a small stream, dripping onto the material while it is being agitated, etc., but the spray method is preferred as providing an efficient means to obtain a relatively uniform distribution of the components in the mixture. Small amounts of the known additives to detergent formulations such as sodium carboxymethyl cellulose, dyes, perfumes, and the like, can be incorporated in the mixture of alkali metal salts to provide a complete detergent formulation.

The following examples are illustrative of this invention:

Example 1

A quantity of dodecylbenzene sulfonic acid prepared by the 100% sulfuric acid sulfonation of dodecylbenzene was diluted by the addition of 20 percent by weight of water and held at about 40°C during the addition of 2 percent by weight of a 30% hydrogen peroxide solution while maintaining mild agitation. The reaction mixture was held at about 40°C for about one-half hour and then cooled to room temperature. The original dodecylbenzene sulfonic acid was a black fluid, which was visually opaque at a depth of about one-quarter inch in a 50-ml Nessler tube, whereas the bleached acid was still of blif.

Example 2

A quantity of commercial dodecylbenzene sulfonic acid containing approximately 10 percent by weight of spent sulfuric acid (80%) was charged into a jacketed, vented reaction vessel equipped with an efficient agitation means. The variable-speed stirrer was turned on and 10 percent by weight of cold water at 20°C was added to the vessel. The temperature was held at between 45-45°C, and 2 percent by weight of a 30% hydrogen peroxide solution was slowly added thereto over a period of 5 minutes. Rapid agitation was continued for 5 minutes after all of the hydrogen peroxide had been added then slow agitation was continued for two hours. It was observed that the black opaque sulfonic acid was bleached to a clear, light yellow fluid.

Example 3

In a similar experiment to Example 2, but treating sulfur trioxide-sulfonated material and using 1 percent by weight of a 30% solution of hydrogen peroxide the sulfonic acid color was maintained for about 15 minutes to one-half hour at 40°C to 55°C and can be aged thereafter at room temperature for about 12-24 hours or more prior to stabilization. In order to be assured of maximum freedom from color in the final detergent composition the sulfonic acid should be bleached while it is still relatively fresh and preferably should be neutralized soon after the bleaching operation is completed. The sulfonic acid can be directly neutralized with an alkali metal hydroxide such
Two hundred twenty-five parts by weight of water was added to 1500 parts by weight of a sample of dodecylbenzene sulfonic acid, which was prepared by the sulfonation of dodecylbenzene with 100% sulfuric acid. The acid was stirred during the addition of the water to effect a uniform temperature of the material. The temperature was adjusted to about 40° C. and held therein during the slow addition of 50 parts by weight of a 30% solution of hydrogen peroxide while maintaining moderate stirring to avoid local overheating. Stirring was continued for about two hours after the addition of the hydrogen peroxide. The acid was diluted to a 5-percent solution and transmission data obtained indicated an improvement of from about 22 percent for the untreated acid to about 70 percent for the treated acid.

Example 5

Two thousand parts by weight of a very dark sample of dodecylbenzene sulfonic acid was introduced into the reaction vessel and 150 parts by weight of water was added thereto while agitating the material. Thereafter about 67 parts by weight of a 30% solution of hydrogen peroxide was slowly added thereto with agitation and the temperature was held at from about 40° to about 50° C. Agitation was continued for 5 minutes and then the treated dodecylbenzene sulfonic acid was cooled and held at between about 20° to 25° C. Transmission data was obtained using a 5-percent solution of acid in the cell. The untreated acid had a transmission of about 32 percent. The treated acid had an initial transmission of about 66 percent and continued to slowly improve over a period of about 3 days when the maximum transmission of about 84 percent was obtained.

Example 6

A typical example of retaining the desirable low color of the bleached dodecylbenzene sulfonic acid by prompt neutralization thereof is afforded by the “dry” neutralization process of directly preparing dry, free-flowing detergent compositions. Twenty-five parts by weight of the freshly bleached dodecylbenzene sulfonic acid was heated to 60° C. and sprayed onto a mixture of finely divided anhydrous alkali metal salts, consisting of 40 parts by weight of sodium tripolyphosphate, 20 parts by weight of sodium carbonate, and 10 parts by weight of sodium metasilicate, while they were being agitated in a ribbon mixer and thereafter blended for about 5 minutes to assure a uniform distribution of the various components in the formulation. Thereafter 5 parts by weight of water was sprayed onto the agitating mixture and agitation continued for about 5 minutes. Then the composition was aged for about one hour to permit the hydration of the salts and subsequently screened to reduce any agglomerated particles. This free-flowing detergent composition had an excellent white color and gave a reflectance measurement of greater than 77 percent.

Whereas the aforesaid illustrative examples are directed to a batch process it should be understood that the process is equally adaptable to a continuous process.

1. The process of bleaching monoalkylbenzene sulfonic acids wherein the alkyl group contains from 9 to 22 carbon atoms comprising the addition of up to 20 percent by weight of water to the sulfonic acid, effects a substantially uniform mixture thereof and adjusting the temperature of the sulfonic acid solution to from about 40° to about 60° C., thereafter adding up to 5 percent by weight, based on the sulfonic acid, of a 30% solution of hydrogen peroxide and effecting rapid distribution thereof in the sulfonic acid by suitable agitation while maintaining the temperature of the sulfonic acid at from about 40° to about 60° C. for at least about one-half hour.

2. The process of claim 1 wherein the bleached monoalkylbenzene sulfonic acid is stabilized by the addition of from about 1 to about 2 percent by volume of a saturated solution of sodium bisulfite at from about 0.5 to about 24 hours after the addition of the hydrogen peroxide to the sulfonic acid.

3. The process of bleaching monoalkylbenzene sulfonic acids wherein the alkyl group contains an average of from about 9 to about 15 carbon atoms comprising the addition of from about 5 to about 10 percent by weight of water to the sulfonic acid, effecting a substantially uniform mixture thereof and adjusting the temperature of the sulfonic acid solution to from about 40° to about 55° C., thereafter adding from about 1 to about 3 percent by weight, based on the sulfonic acid, of a 30% solution of hydrogen peroxide and effecting rapid distribution thereof in the sulfonic acid by suitable agitation while maintaining the temperature of the sulfonic acid at from about 40° to about 55° C. for at least one-half hour.

4. The process of claim 3 wherein the sulfonic acid is dodecylbenzene sulfonic acid prepared by the sulfonation of the alklylation reaction product of a tetrapropylene with benzene in the presence of a Friedel-Crafts catalyst.

5. The process of bleaching a composition consisting essentially of dodecylbenzene sulfonic acid prepared by the sulfonation of the Friedel-Crafts alkylation reaction product of a tetrapropylene with benzene comprising the addition of water to the sulfonic acid composition to adjust the water content thereof to contain up to about 20 percent by weight of water, effecting a substantially uniform mixture thereof and adjusting the temperature of the sulfonic acid solution to from about 40° to about 55° C., thereafter adding from about 1 to about 3 percent by weight, based on the sulfonic acid, of a 30% solution of hydrogen peroxide and effecting rapid distribution thereof in the sulfonic acid by suitable agitation while maintaining the temperature of the sulfonic acid at from about 40° to about 55° C. for at least about one-half hour.

6. The process of claim 5 wherein the bleached dodecylbenzene sulfonic acid is stabilized by the addition of from about 1 to about 2 percent by volume of a saturated solution of sodium bisulfite at from about 0.5 to about 24 hours after the addition of the hydrogen peroxide to the sulfonic acid.

7. The process of claim 5 wherein the bleached dodecylbenzene sulfonic acid is neutralized by the addition of a substantially equivalent quantity of an alkali metal hydroxide at from about 0.5 to about 24 hours after the addition of the hydrogen peroxide to the sulfonic acid.

8. The process of claim 7 wherein the alkali metal hydroxide is potassium hydroxide.

9. The process of claim 7 wherein the alkali metal hydroxide is potassium hydroxide.

10. The process of claim 5 wherein the bleached dodecylbenzene sulfonic acid is neutralized by the uniform addition thereof to a pulverulent mixture of anhydrous alkali metal detergent builder salts selected from the group consisting of sodium carbonate, sodium bicarbonate, sodium tripolyphosphate, tetrasodium pyrophosphate, sodium metasilicate, potassium tripolyphosphate and tetrapotassium pyrophosphate, said neutralization being accelerated by the addition of a fine spray of water to the agitated mixture in an amount not to substantially exceed a total water content in the composition which is equivalent to the amount of water which may be held by the anhydrous alkali metal detergent builder salts as hydrates, and the neutralized dodecylbenzene sulfonic acid composition is characterized by a reflectance of at least about 70 percent.

11. The process of claim 10 wherein 25 parts by
weight of dodecylbenzene sulfonic acid is neutralized by
the spray addition thereof onto a pulverulent mixture
of anhydrous builders consisting of 40 parts by weight
sodium tripolyphosphate, 20 parts by weight sodium car-onate, and 10 parts by weight sodium metasilicate, in a
ribbon mixer and subsequently adding 5 parts by weight
of water as a spray thereto and continuing the mixing
operation for at least about 5 minutes and thereafter
aging for at least about one hour before screening.

References Cited in the file of this patent

<table>
<thead>
<tr>
<th>Patent Number</th>
<th>Inventor</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,842,884</td>
<td>Taylor</td>
<td>Jan. 26, 1932</td>
</tr>
<tr>
<td>2,049,975</td>
<td>Reichert</td>
<td>Aug. 4, 1946</td>
</tr>
<tr>
<td>2,524,056</td>
<td>Jepersen</td>
<td>Oct. 3, 1950</td>
</tr>
<tr>
<td>2,806,055</td>
<td>Feignier</td>
<td>Sept. 10, 1957</td>
</tr>
</tbody>
</table>