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SULFONIC ACID BLEACHING PROCESS

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This invention is directed to a process for improving the color of aliphatic hydrocarbon substituted benzene sulfonic acids. More specifically, the invention is directed to a process for bleaching aliphatic hydrocarbon substituted benzene sulfonic acids with hydrogen peroxide under specifically defined conditions.

In conventional processes for the production of aliphatic hydrocarbon substituted benzene sulfonic acids, products are often obtained which produce dark colored solutions. In a number of uses for the aliphatic hydrocarbon substituted benzene sulfonic acids, for example, in shampoos or as textile assistants, this dark color constitutes a disadvantage, primarily in that the appearance of the products is adversely affected.

The bleaching of sulfonates for improvement of color is a well-known art. Generally, the procedures for bleaching of aliphatic hydrocarbon substituted benzene sulfonic acids involve treatment of their sodium salts in the form of aqueous solutions with sodium hypochlorite.

An object of the present invention is to provide an efficient and economical process for bleaching aliphatic hydrocarbon substituted benzene sulfonic acids with hydrogen peroxide. Other objects and advantages of the invention will be apparent from the following description and examples.

We have discovered that aliphatic hydrocarbon substituted benzene sulfonic acids may be effectively bleached in a bleaching medium consisting of a low amount of hydrogen peroxide and a certain, minimum amount of water diluent. The bleaching operation is carried out by treating the sulfonic acid with not more than about 1% of its weight (100% basis) of hydrogen peroxide in the presence of at least about 8% of its weight of water. Stated otherwise, the low amount of hydrogen peroxide, is, according to the invention, effective in aqueous hydrogen peroxide solutions containing not above about 11.5% by weight of hydrogen peroxide. With aqueous peroxide solutions of higher concentrations, the peroxide fails to effect satisfactory bleaching of the acid and, in some instances, even results in darkening of it.

This hydrogen peroxide bleaching process has the advantage over hypochlorite bleaching processes in that it produces solutions having a lighter color and avoids introduction of inorganic salts which are undesirable in many cases. Further, by treating the free acids of the aliphatic hydrocarbon substituted benzene sulfonic acids, instead of their sodium salts, in the presence of the specified minimum quantity of water, the hydrogen peroxide requirements are greatly reduced.

The aliphatic hydrocarbon substituted benzene sulfonic acids which may be bleached by the process of the present invention include benzene sulfonic acids substituted with aliphatic hydrocarbon radicals containing up to about 23 carbon atoms. Among such substituted benzene sulfonic acids are those derived from dodecylbenzene, long-chain polyalkylated benzenes (by-product from manufacture of dodecylbenzene), keryl benzenes (keryl represents

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a mixture of alkyl groups generally containing from 12 to 16 carbon atoms) and toluene.

The hydrogen peroxide, employed as bleaching agent in the present invention, may be introduced as an aqueous solution in which the hydrogen peroxide constitutes about 1 to 30% by weight of the solution. The amount of hydrogen peroxide employed in practice of the invention is only from about 0.1 to about 1% (100% basis) based on the substituted benzene sulfonic acid being treated. Preferably, a hydrogen peroxide concentration of about 0.2 to about 0.5% (100% basis) based on the sulfonic acid is employed.

In place of the hydrogen peroxide solution, any solution which produces hydrogen peroxide under the bleaching conditions of the present invention may be employed. For example, a solution containing a metal peroxide such as sodium peroxide and an acid such as sulfuric acid may be suitably used.

In order to attain the desired results of the present invention, the presence of a quantity of water at least about 8% by weight of the sulfonic acid being treated is required. Part or all of the water requirement may be satisfied by the water present in the aqueous hydrogen peroxide solution added as bleaching agent. Irrespective of the manner of water addition, the final aqueous peroxide solution will not contain more than about 11.5% by weight of hydrogen peroxide. Generally speaking, amounts of water as high as about 300% by weight of the initial sulfonic acid may be employed. However, with aliphatic hydrocarbon substituted benzene sulfonic acids which are primarily oil-soluble, such as those derived from long-chain polyalkylated benzenes, it is preferred to maintain the water concentration as close to the specified minimum as possible.

We have found that particularly outstanding results have been obtained by using about 8% to about 15% of water by weight of the sulfonic acid being treated. This range of water permits effective bleaching, causes no mechanical difficulties such as gelling of the sulfonic acid and does not dilute the sulfonic acid to a possibly corrosive range.

We have also discovered that part or all of the water diluent required for successful operation of the bleaching process of the present invention may be replaced by alcohols containing from 1 to 3 carbon atoms per molecule. Particularly suitable alcohols include methanol, ethanol, isopropanol and ethylene glycol. Use of these diluents is particularly advantageous when treating materials such as dodecylbenzene sulfonic acid since they are often used in procedures for the extraction of dodecylbenzene sulfonic acid from sulfonation reaction products.

The bleaching procedure of the present invention is generally carried out at temperatures ranging from about 20 to 85° C. Particularly outstanding results have been obtained at temperatures of about 45 to 65° C. After addition of the hydrogen peroxide, the ultimate bleaching desired is attained by aging the treated solution at a temperature of about 30 to 60° C. for about ¼ hour to about 3 hours. However, if desired, a shorter or longer aging period can be used.

When the aliphatic hydrocarbon substituted benzene sulfonic acid is prepared by an oleum or sulfuric acid sulfonation, the resulting product, upon standing, forms two layers, the top layer comprising mainly the sulfonic acid and the bottom layer comprising mainly sulfuric acid. It is a feature of the present invention that when used in conjunction with a sulfonation process which yields spent sulfuric acid, the spent sulfuric acid layer as well as the sulfonic acid layer are both bleached. This is of economic importance since the spent sulfuric acid layer may then be employed for other uses where color is an important consideration.

The present invention may be illustrated by the following examples in which parts are by weight:

EXAMPLE 1

Dodecylbenzene sulfonic acid was prepared by the continuous sulfonation of dodecylbenzene with vaporized sulfur trioxide mixed with diluent air. This sulfonic acid was treated with 2% by weight of water to convert any anhydrides present to the corresponding acids in accordance with the process of Carlson et al. application Serial No. 456,062, filed September 14, 1954.

100 part samples of the treated sulfonic acid (98% concentration) were then diluted further with varying amounts of water at 50 to 55° C. 0.75 part of 30% hydrogen peroxide solution (0.225 part of hydrogen peroxide on 100% basis) was added to each sample (except a blank) with stirring. The samples were then aged at temperatures varying from 50 to 55° C. for about 1 to 2 hours.

The resultant bleached solutions were neutralized by addition of dilute aqueous caustic soda solution to form 10% by weight solutions of dodecylbenzene sodium sulfonate. Comparative colors were then determined on a Klett-Summerson photo-electric colorimeter, test tube model, using No. 42 blue filter, a lower number corresponding to a lighter color. Data for these tests are summarized in Table I below:

Table I

Water Added (Parts)	Total Water Present (Percent by Wt. of Sulfonic Acid)	Temperature, ° C.		Color (After Neutral- ization)
		Bleaching	Aging	
0.....	2.0 (no H ₂ O ₂ added) ¹	50-55	50-55	322
0.....	2.6.....	50-55	50-55	440
8.....	10.7.....	50-55	50-55	153
12.....	14.8.....	50-55	50-55	135
16.....	18.9.....	50-55	50-55	137

¹ Blank.

As shown by the above table, the addition of 30% hydrogen peroxide solution without prior dilution with water actually resulted in a darker product instead of bleaching.

EXAMPLE 2

Tests were carried out by procedure similar to that of Example 1, using 100 parts of 99.5% dodecylbenzene sulfonic acid and varying amounts of water. In each test (except a blank) the amount of hydrogen peroxide constituted about 0.3 part (100% basis). The data for these tests are summarized in Table II below:

Table II

Water Added (Parts)	Total Water Present (Per- cent by Weight of Sulfonic Acid)	Temperature, ° C.		Color (After Neutral- ization)
		Bleaching	Aging	
0.....	0.5 (no H ₂ O ₂ added) ¹	about 40°	30-40° (3 hrs.)	565
0.....	1.2.....	do.....	do.....	610
4.8.....	6.0.....	do.....	do.....	325
6.8.....	8.0.....	do.....	do.....	210
11.0.....	12.2.....	do.....	do.....	200
14.0.....	15.2.....	do.....	do.....	195

¹ Blank.

These tests emphasize the criticality of the minimum concentration of water required by the process of the present invention.

EXAMPLE 3

Tests were carried out in accordance with the procedure of Example 1, using 100 parts of 98% dodecylbenzene sulfonic acid (prepared as in Example 1) and varying strengths of hydrogen peroxide. In each test (except a blank) the amount of hydrogen peroxide con-

stituted about 0.225 part (100% basis). The data for these tests are summarized in Table III below:

Table III

Water Added Prior to Peroxide (Parts)	Hydrogen Peroxide		Total Water Present (Percent by Wt. Sulfonic Acid)	Temperature, ° C.		Color (After Neutral- ization)
	Strength (Percent)	Parts		Bleach- ing	Aging	
10.....	1.0	0	12.2	50-55	50-55	377
9.....	3.0	0.75	11.7	50-55	50-55	142
8.5.....	1.5	1.5	12.0	50-55	50-55	139
7.....	7.5	3.0	12.0	50-55	50-55	153
4.....	3.8	6.0	12.0	50-55	50-55	141
0.....	1.9	12.0	14.1	50-55	50-55	136

¹ Blank.

These tests show that the strength of the peroxide added is immaterial as long as the required amounts of water and peroxide are present. Further, the tests show that the water diluent may be added simultaneously with the hydrogen peroxide (instead of before, as in Examples 1 and 2).

EXAMPLE 4

Tests were carried out in accordance with the procedure of Example 1, using 100 parts of 98% dodecylbenzene sulfonic acid (prepared as in Example 1) and varying quantities of 15% hydrogen peroxide solution. The data for these tests are summarized in Table IV below:

Table IV

Water Added Prior to Peroxide (Parts)	Hydrogen Peroxide (Parts)		Total Water Present (Percent by Wt. Sulfonic Acid)	Temperature, ° C.		Color (After Neutral- ization)
	Gross	Net		Bleaching	Aging	
6.....	4	0.60	11.6	50-55	50-55	118
7.....	3	0.45	11.7	50-55	50-55	113
7.5.....	2.5	0.38	11.8	50-55	50-55	132
8.....	2	0.30	11.9	50-55	50-55	129
8.5.....	1.5	0.23	12.0	50-55	50-55	163
9.....	1	0.15	12.1	50-55	50-55	161
10.....	0	0	12.2	50-55	50-55	450

¹ Blank.

The tests of this example show that the best improvement in reduction of color of dodecylbenzene sulfonic acid occurs when the quantity of hydrogen peroxide used comprises at least about 0.3 part (100% basis) per 100 parts of dodecylbenzene sulfonic acid.

EXAMPLE 5

Dodecylbenzene was sulfonated batchwise with sulfur trioxide vapor. The resultant sulfonic acid was treated with 2% by weight of water to convert any anhydrides present to the corresponding acids.

100 parts of the 98% sulfonic acid were then treated with 8 parts water and 3 parts of 10% hydrogen peroxide solution at 55° C. and aged at 40° C. for about 2½ hours. The quantity of hydrogen peroxide used was 0.3% (100% basis) by weight of the sulfonic acid, and the total water present was about 13% by weight of the sulfonic acid.

The initial sulfonic acid, after neutralization to a 10% solution with dilute caustic soda solution, gave a color of 236 on the Klett-Summerson photo-electric colorimeter, while the hydrogen peroxide-treated sulfonic acid, after neutralization to a 10% solution, gave a color of 63.

EXAMPLE 6

Part A.—1 part of 30% hydrogen peroxide solution was added to a mixture of 42 parts of dodecylbenzene sulfonic acid and 37 parts of 96% sulfuric acid at room temperature. The quantity of hydrogen peroxide used

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was 0.7% (100% basis) by weight of the sulfonic acid, and the total water present was about 5% by weight of the sulfonic acid and about 2.5% by weight of the sulfonic and sulfuric acids. Immediately, the mixture became darker and remained so on standing at room temperature.

Part B.—A mixture of 42 parts of dodecylbenzene sulfonic acid and 37 parts of 96% sulfuric acid was treated with 15 parts of water and allowed to cool to room temperature. Then, 1 part of 30% hydrogen peroxide solution was added. The quantity of hydrogen peroxide used was 0.7% (100% basis) by weight of the sulfonic acid, and the total water present was 41.5% by weight of the sulfonic acid and 19.5% by weight of the sulfonic and sulfuric acids. The mixture immediately became lighter. Upon standing, two layers formed, the top layer comprising primarily the sulfonic acid and the bottom layer comprising primarily sulfuric acid. Both layers were amber in color, being substantially lighter in color than before the treatment with hydrogen peroxide.

EXAMPLE 7

Toluene sulfonic acid was prepared by the direct addition of liquid sulfur trioxide to toluene. The resulting product contained about 10% by weight of ditolyl sulfone.

Part A.—50 parts of the toluene sulfonic acid were treated with 1 part of 30% hydrogen peroxide solution at 30° C. The quantity of hydrogen peroxide used was 0.6% (100% basis) by weight of the sulfonic acid, and the total water present was about 1.5% by weight of the sulfonic acid. The treated sample was allowed to stand overnight, diluted with 449 parts of water and filtered to remove insoluble sulfone. The filtrate was tested for color on the Klett-Summerson photo-electric colorimeter and was found to be 330.

Part B.—50 parts of the sulfonic acid, treated as in part A but in the absence of hydrogen peroxide, exhibited a color value of 350, indicating that little bleaching was effected by the hydrogen peroxide treatment.

Part C.—50 parts of the sulfonic acid were first treated with 5 parts of water and then with 1 part of 30% hydrogen peroxide solution at 30° C. The quantity of hydrogen peroxide used was 0.6% (100% basis) by weight of the sulfonic acid, and the total water present constituted 11.5% by weight of the sulfonic acid. Dilution and color determination as in part A gave a value of 242, showing that considerable bleaching had taken place.

EXAMPLE 8

2 parts of distillation residues, obtained as a by-product in the manufacture of "dodecylbenzene detergent alkylate," were diluted with 1 part of "Procoil A" (a highly solvent-extracted petroleum lubricating oil) and were then sulfonated with sulfur trioxide vapor.

Part A.—50 parts of the resultant sulfonic acid, after dilution with 6 parts of water and 16 hours' aging at room temperature, was diluted with a solvent comprising 50% hexane and 50% isopropanol at a dilution ratio of 16 parts of solvent mixture to 1 part of sulfonic acid. A color value of 825 on the Klett-Summerson photo-electric colorimeter was obtained.

Part B.—50 parts of the sulfonic acid were treated with 1 part of 30% hydrogen peroxide solution at room temperature. The amount of hydrogen peroxide used was about 0.9% (100% basis) by weight of the sulfonic acid, and the total water present constituted about 1.5% by weight of the sulfonic acid. The treated sulfonic acid was then diluted and its color determined as in part A. A value of 640 was obtained, showing that very little bleaching had occurred.

Part C.—50 parts of the sulfonic acid were treated with 5 parts of water, then with hydrogen peroxide solution in the same manner as in part B. The amount of hydrogen peroxide used was the same as used in part B, and the

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total water present constituted about 11.5% by weight of the sulfonic acid. After dilution as in part A a color of 282 was obtained.

EXAMPLE 9

100 part samples of dodecylbenzene sulfonic acid containing 0.5% water were diluted with various alcohols and, in some cases, also with water at about 40° C. 1 part of 30% hydrogen peroxide solution (0.3 part of hydrogen peroxide on 100% basis) was added to each sample (except a blank) with stirring. The samples were then aged at temperatures varying from about 30 to 40° C. for about 2½ hours.

The resultant bleached solutions were neutralized in accordance with Example 1, and comparative colors were determined on the Klett-Summerson photo-electric colorimeter. The following results were obtained:

Table V

Water Added (Parts)	Alcohol Added (Parts)	Total Water+Alcohol Present (Percent by Weight of Sulfonic Acid)	Temperature, ° C.		Color (After Neutralization)
			Bleaching	Aging	
0	0	0.5 (no H ₂ O ₂ added). ³	about 40°	30-40° (2½ Hrs.)	530
0	0	1.2	do	do	630
10	0	11.2	do	do	175
5	1.5	11.2	do	do	166
0	1.10	11.2	do	do	195
0	2.10	11.2	do	do	150

¹ Isopropanol.

² Methanol.

³ Blank.

The above tests illustrate that alcohols containing from 1 to 3 carbon atoms per molecule may be substituted for the water employed in the bleaching process of the present invention.

EXAMPLE 10

Tests were carried out in accordance with the procedure of Example 9, using 100 parts of 99.5% dodecylbenzene sulfonic acid, 1 part of 30% hydrogen peroxide solution (except a blank) and varying quantities of ethanol diluent. The data for these tests are summarized in Table VI below:

Table VI

Water Added (Parts)	Ethanol Added (Parts)	Total Water and Ethanol Present (Percent by Weight of Sulfonic Acid)	Temperature, ° C.		Color (After Neutralization)
			Bleaching	Aging	
0	0	0.5 (no H ₂ O ₂ added). ¹	about 40°	30-40° (2 hrs.)	650
0	1	2.2	do	do	650
0	4	5.2	do	do	440
0	10	11.2	do	do	250

¹ Blank.

The above tests show that approximately the same quantities of alcohol as water are required for effective sulfonic acid bleaching.

Since various changes and modifications may be made in the invention without departing from the spirit thereof, the invention is deemed to be limited only by the scope of the appended claims.

We claim:

1. A process for bleaching a benzene sulfonic acid substituted with an aliphatic hydrocarbon radical containing up to about 23 carbon atoms which comprises treating said acid at a temperature of about 20° to 85° C. in a bleaching medium consisting of hydrogen peroxide and at least one member of the group of diluents consisting of water and alcohols containing from 1 to 3 carbon atoms per molecule, the amount of hydrogen peroxide being about 0.1% to about 1.0% by weight (100% basis) of the acid

and the amount of diluent being at least about 8% by weight of the acid.

2. A process for bleaching a benzene sulfonic acid substituted with an aliphatic hydrocarbon radical containing up to about 23 carbon atoms which comprises treating said acid at a temperature of about 20° to 85° C. in a bleaching medium consisting of hydrogen peroxide and water, the amount of hydrogen peroxide being about 0.1% to about 1.0% by weight (100% basis) of the acid and the amount of water being at least about 8% by weight of the acid.

3. A process for bleaching dodecylbenzene sulfonic acid which comprises treating said acid at a temperature of about 20° to 85° C. in a bleaching medium consisting of hydrogen peroxide and water, the amount of hydrogen peroxide being about 0.1% to about 1.0% by weight (100% basis) of the acid and the amount of water being at least about 8% by weight of the acid.

4. A process for bleaching dodecylbenzene sulfonic acid which comprises treating said acid at a temperature of about 20° to 85° C. in a bleaching medium consisting essentially of hydrogen peroxide and an alcohol containing from 1 to 3 carbon atoms per molecule, the amount of hydrogen peroxide being about 0.1% to about 1.0% by weight, (100% basis) of the acid and the amount of alcohol being at least about 8% by weight of the acid.

5. A process for bleaching a benzene sulfonic acid substituted with an aliphatic hydrocarbon radical containing up to about 23 carbon atoms which comprises treating

said acid at a temperature of about 20° to 85° C. in a bleaching medium consisting of hydrogen peroxide and water, the amount of hydrogen peroxide being about 0.2% to about 0.5% by weight (100% basis) of the acid and the amount of water being about 8% to about 15% by weight of the acid.

6. A process for bleaching dodecylbenzene sulfonic acid which comprises treating said acid at a temperature of about 20° to 85° C. in a bleaching medium consisting of hydrogen peroxide and water, the amount of hydrogen peroxide being about 0.2% to about 0.5% by weight (100% basis) of the acid and the amount of water being about 8% to about 15% by weight of the acid.

7. A process for bleaching dodecylbenzene sulfonic acid which comprises treating said acid at a temperature of about 20° to 85° C. in a bleaching medium consisting of hydrogen peroxide and an alcohol containing from 1 to 3 carbon atoms per molecule, the amount of hydrogen peroxide being about 0.2% to about 0.5% by weight (100% basis) of the acid and the amount of alcohol being about 8% to about 15% by weight of the acid.

References Cited in the file of this patent

UNITED STATES PATENTS

1,842,884	Taylor	Jan. 26, 1932
2,049,975	Reichert et al.	Aug. 4, 1946
2,524,056	Jespersen	Oct. 3, 1950