United States Patent Office 2,805,249 Patented Sept. 3, 1957

2,805,249

PROCESS FOR HYDROLYZING SULFONIC ACID ANHYDRIDES

Everett E. Gilbert, Morris Township, Morris County, and Benjamin Veldhuis, Morristown, N. J., assignors to Allied Chemical & Dye Corporation, New York, N. Y., a corporation of New York

No Drawing. Application September 14, 1954, Serial No. 456,061

6 Claims. (Cl. 260—505)

This invention relates to an improved process for hydrolyzing alkyl aromatic hydrocarbon sulfonic acid anhydrides, and more particularly to an improved process for neutralizing alkyl aromatic hydrocarbon sulfonic acids contaminated with small quantities of anhydrides of such acids.

It is known that alkyl aromatic sulfonic acid anhydrides are extremely resistant to hydrolysis. Thus, according to the literature, p-toluene sulfonic acid anhydride requires 45 minutes in boiling water (100° C.) to effect its solution, i. e. its hydrolytic breakdown to the soluble acid form. (Field, J. Amer. Chem. Society 74, 396, January 20, 1952). Moreover, hydrolysis of anhydrides does not occur rapidly in the conventional caustic neutralization of alkyl aromatic sulfonic acid detergent materials containing such anhydrides, although water is present in large excesses in such neutralization procedures.

It is known to sulfonate long chain alkyl aromatic hydrocarbons including long chain alkyl benzene hydrocarbons such as, for example, dodecylbenzene and dodecyltoluene "detergent alkylates," with sulfur trioxide vapor, either alone or diluted with an inert gas such as air or nitrogen, for example, as described by Gilbert et al., Ind. and Eng. Chem. 45, 2067 (September 1953), to produce detergent products. The resulting hydrocarbon sulfonic acids, when neutralized, as for example, with aqueous sodium hydroxide solutions, to produce sodium salts of the long chain alkyl aromatic hydrocarbon sulfonic acids, which, in solution in water, exert their well known detergent action, unfortunately, often produced turbid solutions when dissolved in water. Furthermore, such neutralized slurries tended to become acid on standing, sometimes after a matter of hours, sometimes not until days or even weeks had elapsed. In order to produce a stable product of the desired pH (7–11), such slurries required one or more reneutralizations after periods of storage. This troublesome reversion of the neutralized slurry was known as "acid drift" or "pH drift" and in many cases was a strong deterrent to the use of the otherwise advantageous direct SO_3 sulfonation processes since the required storage periods prior to reneutralization were not only time consuming but the intermediate redevelopment of acidity in the stored slurry gave rise to excessive equipment corrosion. The difficulty could not be avoided by immediate drying and processing of the neutralized slurry, since such dried products contained the insoluble, turbidity-producing material which made them unsuitable for incorporation into liquid detergents, and since, if incorporated into solid detergents, they were objectionable because of their instability and their gradual development of acidity upon standing.

The above difficulties were found to be due to the presence of water-insoluble long chain alkyl aromatic hydrocarbon sulfonic acid anhydrides $(RSO_2)_2O$; turbidity being due to the existence of the liquid anhydride particles suspended in the solution, the development of

acidity being due to the slow hydrolysis of the anhydrides to the corresponding acids.

Efforts to hydrolyze the anhydrides of these alkyl aromatic hydrocarbon sulfonic acids existing in association with the corresponding acids, by drowning such mixtures in water, i. e. by adding the sulfonic acids to a large excess of water, at room temperatures, or even at temperatures up to 40–50° C., failed to hydrolyze or dissolve the water-insoluble anhydrides.

It was found, that the long chain alkyl aromatic hydrocarbon sulfonic acid anhydrides in the thus neutralized slurries required, for rapid hydrolysis, a heating period, at elevated temperatures of about 80° C., of about a half hour or more.

While the conventional long chain alkyl aromatic hydrocarbon sulfonic acid neutralization reaction is, of course, exothermic, the magnitude of the heat of reaction is not sufficient to cause hydrolysis, and moreover, in general the temperature of the neutralization of such acids is usually controlled to prevent its rise above about 60° C. to avoid degradation of the resulting product. Therefore, such heat treatments would not only be costly from a heat input standpoint, and inconvenient, but would also be disadvantageous, first in producing serious discoloration of the sulfonic acids if such heating were carried out in the customary steel tanks, rendering the resulting products inferior or unsatisfactory for use as detergents, and second, in causing serious corrosion of the equipment. In addition, such a heat-treating process causes a large volume increase of the treated slurry; this would necessitate the use of larger and more costly processing equipment.

It is an object of the present invention to provide an improved process for carrying out the hydrolysis of alkyl-aromatic hydrocarbon sulfonic acid anhydrides.

It is a further object to provide a process for accelerating the hydrolysis of such anhydrides.

Another object of the present invention is to provide a rapid, low temperature neutralization process for long chain alkyl aromatic hydrocarbon sulfonic acids which are contaminated with minor quantities of anhydrides of such acids, in which hydrolysis of the anhydrides to the corresponding acids is simultaneously accomplished.

It is a still further object of the invention to provide a process for the acceleration of the hydrolysis of long chain alkyl aromatic hydrocarbon sulfonic acid anhydrides in neutralized slurries of the corresponding sulfonic acids at temperatures within the range of normally employed neutralization temperatures.

A still further object is to provide a process for preparing long chain alkyl aromatic hydrocarbon sodium sulfonate compositions free from "acid drift."

These and other objects are accomplished according to our invention wherein alkyl aromatic hydrocarbon sulfonic acid anhydrides are contacted in an aqueous medium with ammonia or an organic amine at pH values of at least about 7, for periods sufficient to effect hydrolysis of the anhydrides.

In the preparation of long chain alkyl aromatic hydrocarbon sulfonic acids by sulfonation of the hydrocarbon with sulfur trioxide, various factors contribute to the formation of the hydrocarbon sulfonic acid anhydrides from the sulfonic acids formed. Thus, large excesses of SO_3 and low reaction temperatures increase the amounts of anhydrides formed. Employment of one or more of such conditions, however, is often necessary to produce final products having acceptably low oil contents and color, and in attaining these criteria, anhydride contents of as high as about 15% based on the weight of the crude sulfonic acid product are sometimes produced. Anhydride contents, however, are usually somewhat lower, for

example, in the range between about 0.5% and about 9% on the above basis.

The presence or absence of anhydrides in neutralized slurries of long chain alkyl aromatic hydrocarbon sulfonic acids can readily be determined qualitatively by diluting the slurry or a portion thereof to a 10% or less active solution. The resulting solution is turbid if anhydride is present, or clear if anhydride is absent.

Quantitatively, the amount of anhydride can be determined by heating an aqueous solution of the neutralized sulfonic acid product to elevated temperatures of around 80° C. for a period sufficient to effect complete hydrolysis to the acid (usually between about one half hour and about one hour), and neutralizing the acid formed with an alkali such as sodium hydroxide. The quantity of anhydride present is an amount chemically equivalent to the sodium hydroxide used in the reneutralization.

In carrying out the process according to our invention, alkyl aromatic hydrocarbon sulfonic acid anhydrides are hydrolyzed in an aqueous medium containing ammonia or an amine, and in which the pH of the medium is maintained at 7 or above. The pH may be maintained either by the addition of sufficient ammonia or amine to completely neutralize the acids resulting from the hydrolysis, or, preferably, by the use of a smaller quantity of amine together with an inorganic neutralizing agent such as an alkali metal hydroxide or carbonate, for example, sodium hydroxide, in an amount sufficient to neutralize all or a part of the resulting alkyl aromatic sulfonic acid formed by hydrolysis. Long chain alkyl aromatic hydrocarbon sulfonic acids containing anhydrides of such sulfonic acids, which are to be neutralized, as with an alkali metal hydroxide or carbonate, preferably with sodium hydroxide, are treated in the usual way except that a small amount of an amine, as defined, is introduced into the sulfonic acids, either at the same time as the neutralizing agent, or after neutralization to pH 7 or above has been completed. The neutralized slurry is then allowed to remain in contact with the amine for a short time, preferably with agitation and preferably at a slightly elevated temperature not higher than about 60° C., until hydrolysis of the anhydrides to the sulfonic acids is complete.

According to one aspect of our invention as it relates to the treatment of long chain alkyl aromatic hydrocarbon sulfonic acids, neutralized slurries of such acids are first prepared in the conventional manner, adjusted to a pH value of 9 or higher, for example, between about 9 and about 11, and a small quantity of an amine is added to the slurry while continuing its agitation. The pH shift begins to occur, and is accelerated by the presence of the amine. As the pH drops, neutralizing agent is added periodically until the pH shift ceases, then the pH is adjusted to the desired level, usually about 9. In this manner, hydrolysis of the anhydrides, which often requires weeks for completion by simple storage of the slurry, is usually completed in a period of a few hours, usually in not more than about an hour, and without the use of deleteriously elevated temperatures.

In a preferred aspect of the neutralization procedure according to the invention, however, the amine is added to the neutralizing agent, and, as sulfonic acids are introduced into the mixture of amine and neutralizing agent, the amine acts to accelerate hydrolysis of the anhydrides present during the course of the neutralization so that by the time the neutralization step is complete, sufficient time has elapsed (about ½ to 1 hour), so that the hydrolysis has proceeded to an appreciable extent and the time required after the neutralization step for its completion is reduced by perhaps half an hour or more. After hydrolysis is complete the pH is adjusted in the usual way by the addition of neutralizing agent to neutral (7) or above, usually to about 9.

Thus, by either of the above modifications of our process, long chain alkyl aromatic hydrocarbon sulfonic acid alkali metal salt slurries containing anhydrides of such acids, and which normally might require up to several weeks time to reach a state of complete hydrolysis of the anhydrides if simply left standing, can be brought to stable pH values and substantially complete hydrolysis of their anhydride contents effected in periods ranging from about ½ hour to about 5 hours, and without objectionable heating.

Either ammonia or any organic amine is effective to hasten the hydrolysis of the alkyl aromatic hydrocarbon sulfonic acid anhydrides in aqueous media at pH values of 7 or above, as in slurries of alkali metal salts of long chain alkyl aromatic sulfonic acids. Effective amines include ammonia, quaternary ammonium compounds, primary, secondary and tertiary aliphatic amines, aromatic amines, heterocyclic nitrogen base compounds and the like. When the term amine is used herein, it is to be understood to include ammonia and the quaternary ammonium compounds, as well as the organic amines. Certain amines cause greater acceleration of the hydrolysis than others, for example, morpholine, dimethylamine, ethylenediamine and propylenediamine are especially active in accelerating hydrolysis, while pyridine, triethylamine, triethanolamine, hexamethylenediamine, aniline, monoisopropanolamine, propylenediamine, ethylenediamine, aminoethylethanolamine, 1,3-diaminobutane, dimethylaniline, piperidine, cyclohexylamine, benzylamine, acetaldehyde ammonia, 1,3-diamino-2-propanol, diethanolamine, triethanolamine, amylamine, hexamethylenetetramine, ammonia, quinoline, isopropylamine, acetamide, diethylenetriamine, 2-aminopyridine, diethylamine, mixed isopropanolamines, tetraethanolammonium hydroxide, methylamine, N-aminoethyl morpholine, produce marked acceleration of hydrolysis of the sulfonic acids. Other effective amines include triethylene tetramine, tetraethylene pentamine, n-butylamine, isobutylamine, diisobutylamine, n-hydroxyethyl morpholine, 2-(betahydroxyethyl) pyridine, diisopropylamine, phenyldiethanolamine, N-methyl morpholine, N-aminopropyl morpholine, etc.

The quantity of amine necessary to effect an appreciable reduction in the hydrolysis time of the sulfonic acid anhydrides varies somewhat with different amines and with the quantity of anhydride present. In general, larger quantities of amine effect greater accelerations than do smaller quantities. In general, however, quantities of amines between about .01% and about 5% based on the weight of the anhydrides present are sufficient. In the case of long chain alkyl aromatic hydrocarbon sulfonic acid neutralizations, between about 0.1% and about 10% by weight, based on the weight of the sulfonic acids is usually sufficient to produce complete stability and freedom from pH shift, of anhydride-containing slurries, in periods of between about ½ hour and about 5 hours, whereas, in the absence of the amine, the same slurries require periods of between about one week and about one month standing at room temperatures to reach stability. Usually between about ½% and about 2% of amine on the sulfonic acid basis, is preferred for use in the neutralization of such acids.

The following specific examples further illustrate our invention. Parts are by weight except as otherwise noted.

EXAMPLE 1

Dodecylbenzene was sulfonated by passing a mixture of SO_3 and air containing 10% by volume of SO_3 into 420 parts of dodecylbenzene over a period of 30 minutes while maintaining the reaction temperature between 32° C. and 56° C., until 140 parts of SO_3 (a 2.5% excess) had been introduced. Of the resulting 571 parts of dodecylbenzene sulfonic acid product, 463 parts were "neutralized" by adding them to 308 parts of 20% sodium hydroxide solution in 304 parts of water. The thus "neutralized" slurry had a pH of 12.5. The slurry was allowed to stand for 20 minutes, whereupon the pH had dropped to 9. After standing for about 20 hours (overnight), the pH had dropped to 1, indicating the presence of an-

hydrides, and that such anhydrides had partially hydrolyzed to the acids on standing. The pH of a 500 part portion of the slurry was then adjusted to 8 by the addition of sodium hydroxide solution, and heated to about 75–80° C. over a period of about 50 minutes. pH values were noted periodically during heating, and additions of sodium hydroxide were made as necessary to bring the pH back to 8 periodically as it dropped. The course of the test is indicated in Table 1 below:

Table 1

pH DRIFT

Time, Total Elapsed Minutes	Temp., °C.	pH	Ml. 20% NaOH	
			Added	Total
0	30	1	0	0
5	28	8	8	8
10	47	8	0	8
25	77	4→8	1	9
30	81	4→8	1	10
45	88	4→8	1	11
50	81	6→8.5	1	12
60	75	8.5	0	12
70	80	8.0	0	12
115	87	8.0	0	12

It will be observed from the table that the "neutralized" dodecylbenzene sulfonic acids prepared as described above, required heating for at least about an hour at about 75–80° C. with periodic reneutralizations to complete the hydrolysis of the anhydrides present and to produce a stable neutralized product. This test indicated the presence of about 8% dodecylbenzene sulfonic acid anhydride based on the weight of the crude sulfonic acids.

Four 25 part portions of sodium dodecylbenzene sulfonate slurry produced as described above, were diluted with water to form aqueous solutions containing about 10% sodium salt, by dissolving 25 parts of the slurry in 75 parts of water. The solutions all were cloudy, indicating the presence of anhydrides. To each solution thus prepared was added 0.7 part by volume of a 20% NaOH solution, i. e. sufficient NaOH to neutralize the acidity which would be produced by eventual hydrolysis of the anhydride content. One of the four solutions was retained as a control; the remaining solutions were treated with 3 drops, respectively, of pyridine, triethylamine and triethanolamine. The treated solutions were then allowed to stand at about 30° C. and the degrees of clarification of the amine-treated samples as compared to the untreated control were noted. In 25 minutes, the pyridine treated sample appeared slightly darker and clearer than the control, indicating that some of the anhydride had been converted to the corresponding acid. In 70 minutes the pyridine treated sample was much darker, indicating substantial conversion of the anhydride to acid; and, after standing for 4 hours, was almost clear, indicating virtually complete hydrolysis of the anhydride. The samples containing triethylamine and triethanolamine, after standing for 21 hours, had clarified considerably, although hydrolysis apparently was not complete. No noticeable clarification of the control solution took place during the period of the test.

Further tests were carried out on additional diluted, neutralized samples of the above slurry, in a similar manner except that 5 drops of morpholine, hexamethylenediamine, aniline, dimethyl aniline, and ethanolamine respectively were added to the test solutions. After standing 19 hours at room temperature, the test solution containing morpholine was clear, indicating substantially complete hydrolysis of the anhydride. The remaining solutions, at the end of the 19 hours' test period, were appreciably darker, i. e. clearer than the control, indicating substantial acceleration of the hydrolysis by the presence of these amines.

EXAMPLE 2

507 parts of a sodium dodecylbenzene sulfonate slurry produced in the same manner as that described under Example 1, and containing about 6.5% of anhydride, were diluted with water to form an aqueous test solution containing about 10% dodecylbenzene sulfonic acid sodium salt. Portions of this solution were neutralized in the manner described under Example 1 above. A control was retained, and the remaining samples were treated respectively with the amines listed in Table 2 below. The solutions were allowed to stand at least until they began to clarify. The control solution, to which no amine had been added, showed no clarification during the periods of the tests. All the solutions containing one of the amines listed in the table, exhibited accelerated hydrolysis as compared to the control solution, as measured by a greater degree of clarification than the control at the termination of the test. Of the amines listed, morpholine, propylenediamine, ethylene diamine and dimethylamine were especially active, resulting in substantially complete clarification of the solution in 3 hours.

Table 2

AMINES PRODUCING ACCELERATED HYDROLYSIS

Pyridine
Triethylamine
Triethanolamine
Morpholine
Hexamethylenediamine
Aniline
Monoisopropanolamine
Propylenediamine
Ethylenediamine
Aminoethylethanolamine
Benzylamine
Acetaldehyde ammonia
1,3-diamino-2-propanol
Diethanolamine
Amylamine
Hexamethylenetetramine
Ammonia
Quinoline
Isopropylamine
Acetamide
Diethylenetriamine
2-aminopyridine
Diethylamine
Isopropanolamine
Dimethylamine
Mixed isopropanolamine
Tetraethanolammonium hydroxide
Methylamine
N-aminoethyl morpholine
1,3-diaminobutane
Dimethylaniline
Piperidine
Cyclohexylamine

EXAMPLE 3

A sample of dodecyl benzene sulfonic acid prepared in a manner similar to that described in Example 1, except that the sulfonation was carried out at temperatures from 30 to 60° C. for a period of 50 minutes until a molar excess of 5% SO_3 had been added, was tested for the presence and quantity of anhydrides by adding 235 parts thereof to 300 parts of a 10% NaOH solution, producing a pH of 6. An additional 2 parts of NaOH was added to bring the pH to 7. The slurry thus formed was then heated to 70–82° C. for 50 minutes to hydrolyze any anhydride present to the acid while observing the pH periodically. pH drop occurred, and additional NaOH solution was added as necessary after each pH reading, to bring the pH to neutral or above. The solution required 22 grams 10% NaOH solution to bring the pH to a stable condition at pH 9, indicating the presence of

7% dodecyl benzene sulfonic acid anhydrides in the original dodecyl benzene sulfonic acids. A 231 part sample of the above original dodecyl benzene sulfonic acid was added to 300 parts of a 10% aqueous NaOH solution containing 4 parts of monoisopropanolamine, forming a "neutralized" slurry having a pH of 8.5. The temperature during the neutralization was 30–50° C. Immediately after neutralization the slurry was tested for the presence of anhydride as follows: A glass stirring rod (6 mm. diameter) was dipped into the slurry to a depth of about 3 centimeters. The slurry adhering to the rod was then transferred to a few ml. of water contained in a 20 x 150 mm. test tube.

The solution exhibited only a very slight turbidity, indicating only a trace of remaining anhydride. A sample of dodecyl benzene sulfonic acid prepared under the same conditions as those described and similarly neutralized with sodium hydroxide and with no amine present required standing for about a week to produce a clear solution when subjected to the same test.

EXAMPLE 4

228 parts of the dodecylbenzene sulfonic acid prepared as described in Example 3 above, was converted into a slurry by adding it to 308 parts of 10% aqueous sodium hydroxide, producing a pH of 8. Then 2 parts of ethylenediamine were added to the slurry producing a pH of 9. The slurry was then maintained at 40–50° C. for 25 minutes, whereupon the pH remained at 9 and a turbidity test carried out as described in Example 3 indicated that only a trace of anhydride remained. After standing overnight, all anhydride had disappeared as indicated by a clear solution obtained in the turbidity test.

EXAMPLE 5

921 parts of dodecylbenzene sulfonic acid prepared as described under Example 3 were added to 1206 parts of 10% aqueous NaOH. Heat treatment of an aliquot of the slurry as described in Example 3 showed that 500 grams required 15.5 additional grams of a 10% aqueous NaOH solution to completely neutralize the hydrolyzed sulfonic acid anhydrides and to achieve a stable pH at 9, indicating the presence of 5% anhydrides based on the weight of the crude sulfonic acids. Then three 500 gram samples of the slurry were taken and to each was added at room temperature (about 30° C.) a mixture of isopropanolamine and sodium hydroxide in a total amount equivalent to 15.5 grams of 10% aqueous NaOH, the proportion of base supplied by the amine differing in the three samples, being 0.6, 1.2 and 2.4 grams of amine respectively. Samples so treated were maintained at temperatures between about 30° C. and 50° C. and were tested periodically for anhydride content by the turbidity test as described in Example 3. The times required for complete disappearance of anhydride as indicated by a clear solution are shown in Table 3 below.

Table 3

EFFECT OF QUANTITY OF AMINE ON RATE OF ANHYDRIDE BREAKDOWN

	Test 1	Test 2	Test 3
Gms. 10% NaOH	14.5	11.0	5.5
Gms. isopropanolamine	0.6	1.2	2.4
Clarification Time (Hrs.)	19.0	2.5	2.0

This test indicates that increasing the amount of amine increases the acceleration of hydrolysis.

EXAMPLE 6

1028 parts of dodecylbenzene sulfonic acid prepared in a manner similar to that described in Example 3 but using a low excess of SO_3 in the sulfonation (1% excess) were added to 1328 parts of a 10% aqueous NaOH solution, and produced a slurry having a pH of 7.4. Heat treatment of an aliquot of the resulting slurry as described under Example 1, Table 1, showed that 300 grams thereof required 2 grams of 10% aqueous NaOH to neutralize the hydrolyzed sulfonic acid anhydrides and to achieve a clear solution having a stable pH at 9. This slurry therefore had an anhydride content of about 1% by weight based on the weight of the crude sulfonic acids, this being considerably lower than that of the slurry of Example 5. To five 200 gram portions of this slurry, were added small quantities of ethylenediamine, dimethylamine and morpholine respectively, as indicated in Table 4 below, with no additional base, with the result that on standing at 27° C. for the times indicated, complete elimination of anhydride was obtained as indicated by the turbidity test.

Table 4

TIME FOR COMPLETE BREAKDOWN AT 27° C. of ANHYDRIDE IN 200 GRAMS OF AQUEOUS SODIUM DODECYL BENZENE SULFONATE SLURRIES IN PRESENCE OF INDICATED AMOUNTS OF SEVERAL AMINES

Amine	Grams	Wt. Percent Based on wt. of Sulfonic Acid	Time for Clarification
Dimethylamine	0.25	0.3	10 minutes.
Morpholine	0.25	0.3	Do.
Ethylenediamine	0.25	0.3	1.5 hours.
Ethylenediamine	1.00	1.1	10 minutes.
None (10% aqueous NaOH)	1.00		No clarification in 1.5 hours.

EXAMPLE 7

Dodecylbenzene sulfonic acids were prepared in a manner similar to that described under Example 3 in which sulfonation was carried out at 28–56° C. over a period of 47 minutes, an excess of 5% SO_3 being added. 1041 parts of these sulfonic acids were added to 1369 parts of a 10% aqueous NaOH solution. Heat treatment of an aliquot of the resulting slurry at 46–85° C. over a period of an hour showed that 300 grams of slurry required 6.5 grams of 10% aqueous NaOH to achieve stabilization of pH and that there was thus present 4% of anhydrides based on the weight of the sulfonic acids. A series of tests was then made on 200 gram aliquots of the orignal slurry with the addition of various amounts of morpholine, ethylenediamine and dimethylamine, with and without added sodium hydroxide. The slurries were allowed to stand at 28° C. until complete hydrolysis of the anhydride had occurred. Data and time required for clarification of the test solutions (indicative of complete hydrolysis) are given in Table 5 below:

Table 5

Test No.	NaOH 10%, gms.	Amine	gms.	Percent Amine based on wt. of sulfonic acids	Time to Clarify Hours
1	4.8	None			more than 2.
2	0.5	Morpholine	1.0	1.1	Less than 0.25.
3	2.8	do	0.5	0.7	Do.
4	4.2	do	0.25	0.3	more than 2.
5	0.0	Ethylenediamine	1.0	1.1	2.
6	1.7	do	0.5	0.7	more than 2.
7	3.6	do	0.25	0.3	Do.
8	0.0	Dimethylamine	0.8	1.0	less than 0.25.
9	1.5	do	0.4	0.5	1.
10	3.4	do	0.2	0.3	more than 2.

EXAMPLE 8

A slurry of dodecylbenzene sulfonic acid sodium salt, containing about 3% of anhydrides was prepared as described in Example 1. Dilution of the untreated slurry to contain 10% dodecylbenzene sulfonic acid sodium salt was carried out and produced a cloudy solution. To separate, 25 ml. portions of the diluted material were added 2 or 3 drops of one of the amines listed below. The mixtures were allowed to stand at temperatures between

about 30° C. and about 50° C., until the solutions started to clarify, indicating hydrolysis of the anhydrides. The tests were continued for a maximum of 5 hours during which time all had exhibited a substantial degree of clarification. A control sample to which no amine had been added exhibited less clarification in every case than the sample containing amine under similar test conditions.

Table 6

AMINE
N-hydroxyethyl morpholine
n-Butylamine
Isobutylamine
Triethylenetetramine
Tetraethylenepentamine
2-(betahydroxyethyl) pyridine
Diisobutylamine
Diisopropylamine
Phenyldiethanolamine
N-methyl morpholine
N-aminopropylmorpholine

While the above describes the preferred embodiments of our invention, it will be understod that departures may be made therefrom within the scope of the specification and claims.

We claim:

1. A process for the neutralization of long chain alkyl aromatic hydrocarbon sulfonic acids containing between about 0.5% and about 15% by weight, based on the weight of the sulfonic acids, of anhydrides of such acids, which comprises neutralizing the crude sulfonic acids with an aqueous solution of an alkali metal hydroxide at a temperature not substantially in excess of about 60° C. in the presence of between about 0.1% and about 10% by weight based on the weight of the sulfonic acids of an organic amine.

2. The process according to claim 1, wherein the long chain alkyl aromatic hydrocarbon is a long chain alkyl benzene hydrocarbon.

3. The process according to claim 1, wherein the amine is morpholine.

4. The process according to claim 1, wherein the amine is dimethylamine.

5. The process according to claim 1, wherein the amine is ethylenediamine.

6. The process according to claim 1, wherein the amine is propylenediamine.

References Cited in the file of this patent

UNITED STATES PATENTS

2,489,316	Proell	Nov. 29, 1949
2,676,185	Melstrom	Apr. 20, 1954