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STABILIZATION OF PEROXY SOLUTIONS

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This is a conutinuation-in-part of co-pending patent application Ser. No. 231,596, filed October 18, 1962.

This invention relates to methods for stabilizing aqueous peroxy solutions and, more particularly, to methods for bleaching cellulosic materials such as cotton, linen, jute, rayon, paper and the like, using aqueous peroxy solutions having dissolved therein novel stabilizing agents.

It has been reported that peroxide bleaching has supplanted chlorine bleaching to the extent that about 80% of cotton bleaching is done by use of peroxide as a bleaching agent. Also, about all of the continuous bleaching methods use peroxide as the bleaching agent and about 90% of the cotton that is bleached with peroxide is bleached by continuous bleaching methods.

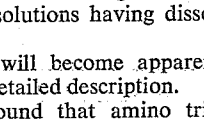
The use of a stabilizing agent to minimize the decomposition of the peroxy compound is well established in the peroxy bleaching art, because, among other things, the oxygen released by decomposition of the peroxy compound in general has no bleaching action as contrasted with the normal autodecomposition of the peroxy compound which does function as a bleaching agent. In fact, the decomposition of the peroxy compound may be harmful. For example, cellulosic materials in strongly alkaline peroxy solutions are attacked by the oxygen from decomposition with the result of loss of strength by the materials. In general, stabilizing agents are of various and diverse nature and the ability of a material to be an effective stabilizing agent is apparently unpredictable. For example, although a few sequestering agents such as sodium pyrophosphate can be considered as stabilizing agents, the majority of sequestering agents are not considered to be effective stabilizing agents while such non-sequestering materials as sodium stannate and sodium silicate have been reported as being effective stabilizing agents. Therefore, due to their unpredictability and their diverse nature, the stabilizing agents for peroxy solutions vary in their ability with changes in the prevailing conditions such as pH, temperature conditions and the like of the peroxy solutions. For today's bleaching conditions the stabilizing agent should preferably be effective in alkaline solutions and under relatively high temperature condtions which are frequently encountered in practice as well as being compatible with other additives usually present in the peroxy bleaching solutions such as optical whiteners, that is, brighteners or fluorescent white dyes, wetting agents and the like.

Therefore, an object of this invention is to provide an improved method for stabilizing aqueous peroxy solutions.

Another object of this invention is to provide an improved method for bleaching cellulosic materials using aqueous peroxy solutions having dissolved therein novel stabilizing agents.

Other objects will become apparent from a reading of the following detailed description.

It has been found that amino tri(lower alkylidenephosphonic acids) or their salts, said acids being of the following formula:



wherein X and Y represent hydrogen or a lower alkyl group (1-4 carbon atoms), are effective stabilizing agents for peroxy solutions as will be more fully discussed hereinafter.

Compounds illustrative of the invention are: amino tri(methylphosphonic acid), amino tri(ethylidenephosphonic acid), amino tri(isopropylidenephosphonic acid), amino mono(methylphosphonic acid) di(ethylidene phosphonic acid, and amino tri(butylidene phosphonic acid).

It is to be understood that although the free acids can be used, the water-soluble salts are preferred, especially the sodium salts of amino tri(lower alkylidenephosphonic acids) and in particular the penta sodium salt has proven to be quite effective. Other alkali metal salts, such as potassium, lithium and the like, as well as mixtures of the alkali metal salts may be used. In addition, any water-soluble salt, such as the ammonium salt (e.g., $N(CH_2PO_3(NH_4)_2)_2(CH_2PO_3HNH_4)$, and the amine salts

(e.g., $N(CH_2PO_3(N(CH_3)_2)_2)_2(CH_2PO_3HN(CH_3)_2)$

which exhibit the characteristics of the alkali metal salt may be also used to practice the invention.

The stabilizing agents of the instant invention exhibit, in addition to their stabilizing ability, the highly beneficial properties of being highly water-soluble and hydrolytically stable, that is, having a substantial resistance to hydrolysis or degradation under various pH and temperature conditions. For example, a 20 gram sample of penta sodium amino tri(methylphosphonate),

$$N(CH_2—PO_3Na_2)_2(CH_2—PO_3HNa)$$

was dissolved in 100 ml. of water. A 25 ml. portion of the solution was added to a 25 ml. portion of 12 M HCl to give a 10% solution of the stabilizing agent in HCl. Another 25 ml. portion of the solution was added to a 25 ml. portion of 10% NaOH to give a 10% solution of the stabilizing agent in a 5% solution of NaOH. The foregoing 10% solutions were boiled for a period of four hours, at the end of which both solutions exhibited no change in physical properties. Nuclear magnetic resonance spectra showed the two 10% solutions to be identical with a fresh 10% solution of the stabilizing agent in water, thereby establishing the resistance of the stabilizing agent to hydrolysis or degradation under severe temperature and pH conditions. It should be noted that all known polyphosphates, whether in the acid, salt or ester form, would hydrolyze or degrade completely under the foregoing conditions.

Peroxy solutions which are capable of being stabilized in addition to hydrogen peroxide and its addition compounds, such as the peroxide of sodium and the super oxide of potassium, include urea percompounds, perborates, persulfates, and the peracids such as persulfuric acid, peracetic acid, peroxy monophosphoric acid and their water-soluble salt compounds such as sodium, potassium, ammonium and organic amine salts.

Depending upon, interalia, the particular peroxy-compound used, the pH of the aqueous peroxy solution is usually adjusted with inorganic alkali metal basic materials, such as sodium hydroxide, sodium carbonate, sodium silicate, di- and tri-sodium phosphates and the like, including mixtures of these as well as the potassium forms of the foregoing materials, to a pH of between about 7.5 and about 12.5. Usually if the pH is higher than about 12.5 rapid bleaching occurs and the peroxy-compounds rapidly decompose so that it is difficult to control a proper bleaching rate without undue damage to the fibers. At pH values lower than about 7.5, the rate of bleaching in most cases is slow to the extent of being uneconomical for bleaching.

The concentration of perxoy solutions can vary depending upon, inter alia, the type of peroxy-compound, pH, temperature, type of bleaching desired and the like, however, normal concentrations, i.e., from about 0.01

to about 5% can be used with concentrations from about .2 to about 3% being preferred.

The stabilizing agents of the present invention may be dissolved in the peroxy solution which is ready for use or may be incorporated in a concentrated peroxy solution, such as a 35% solution of hydrogen peroxide, which is usually further diluted to form the peroxy solution for bleaching. In addition, the stabilizing agent can be incorporated in dry bleach compositions, such as perborate compositions, by admixing therewith, and the resulting composition dissolved in the aqueous system immediately preceding its end use application. In any event, the stabilizing agent is intended to be used with the peroxy solution at the time of its use for bleaching purposes.

The concentration of the stabilizing agent of the present invention in the peroxy solution can vary depending upon, inter alia, concentration of the peroxy solution, type of peroxy-compound used, pH, temperature and the like, and usually for normal concentrations of peroxy solutions and with conventional bleaching methods, the stabilizing agent is preferably present in concentrations from about 0.001 to about 5% with from about 0.1% to about 1% being especially preferred.

The methods for bleaching using the peroxy solutions containing the stabilizing agents of the present invention vary widely, as for example, from using the peroxy solutions at normal temperatures, i.e., from about 20° C. to about 35° C. and contacting the cellulosic material by immersion for periods of time of several hours, i.e., from about 12 to about 36 hours, to using the peroxy solutions at temperatures from about 70° C. to about 100° C. for periods of time from about 30 minutes to about 6–8 hours, as well as continuous bleaching methods which entail the use of the peroxy solutions at normal temperatures, i.e., about 25° C. and contacting the cellulose material by saturation, removing the excess moisture and exposing the cellulose material to saturated steam at temperatures from about 100° C. to about 135° C. for periods of time from a few seconds (about 20) to about 1 hour and even longer in some cases. U.S. Patents 2,839,353, 2,960,383, and 2,983,568 are illustrative of being representative of continuous peroxy bleaching methods.

The amino tri(lower alkylidenephosphonic acids) and their salts may be prepared by various means, one of which comprises as a first step the preparation of the corresponding esters by reacting under reactive conditions ammonia, a compound containing a carbonyl group such as an aldehyde or ketone, and a dialkylphosphite. The free amino tri(lower alkylidenephosphonic acids) and their salts may be prepared by hydrolysis of the esters.

To illustrate the invention, the following examples are presented.

EXAMPLE 1

Into a conventional 3-necked, 3-liter flask fitted with a reflux condenser, stirrer and thermometer was added 600 grams of diethyl phosphite and 127.5 grams of 29% aqueous ammonia solution. The flask was placed in an ice bath and after the mixture had become cooled to about 0° C. 325 grams of 37% aqueous formaldehyde solution was added. The flask was removed from the ice bath and heated with the reaction occurring at above 100° C. After the reaction was completed, the flask was allowed to cool to room temperature and the reaction products were extracted with benzene and separated by fractional distillation. Hexaethyl amino tri(methylphosphonate) distilled between 190°–200° C. at a pressure of .1 mm. and was obtained in a quantity of 184 grams. The following are the results to enable a comparison between the calculated percent constituents and found percent constituents.

Calculated: 36.78% C., 7.30% H, 3.53% N, 20.01% P. Found: 38.54% C, 7.76% H, 3.00% N, 18.89% P.

The free acid, amino tri(methylphosphonic acid), $N(CH_2P(O)(OH)_2)_3$, was prepared by hydrolysis of a portion of the foregoing prepared ester. In a flask similar to that described above 40 grams of the ester was refluxed with about 200 ml. of concentrated hydrochloric acid for a period of about 24 hours. The free acid, a sirupy liquid, crystallized on prolonged standing (about 1 week) in a desiccator. The yield was 20 grams. The equivalent weight of the free acid, by titration, was found to be 62 as compared with the calculated value of 59.8.

EXAMPLE 2

Penta sodium amino tri(methylphosphonate), $N—(CH_2P(O)_3Na_2)_2—(CH_2P(O)_3HNa)$, was prepared by dissolving the free acid obtained in Example 1 in 140 ml. of 10% NaOH solution and evaporating the aqueous solution to dryness at about 140° C. with the anhydrous form of the salt being formed.

It is believed that the amino tri(lower alkylidene phosphonic acids) and their salts are effective stabilizing agents due to, inter alia, their ability to function as sequestering and deflocculating agents in alkaline peroxy solutions and at relatively high temperatures which are frequently encountered in the bleaching art, with the result of inactivating catalytically-active substances, such as iron, copper and manganese which greatly accelerate the decomposition of the peroxy-compound, as well as their ability to be only moderately oxidized by the peroxy solutions during normal periods of time under bleaching conditions frequently encountered.

In order to illustrate the stabilizing ability of the compounds of the instant invention, the following tests were made with the indicated results. The testing procedure used consisted of kinetic runs carried out in a suitable flask, stirred by a vibrating stirrer and thermostated at about 85° C. The flask initially contained one liter of solution of the following typical composition: 1.0% sodium silicate, 0.35% H_2O_2, stabilizing agent as indicated, and 2.5×10^{-5} percent Cu^{++} (as $CuSO_4$). The pH was adjusted to 10.0. The run was started by adding 10 ml. of concentrated peroxide solution to 990 ml. of solution. At intervals, 10 ml. aliquots of solution were withdrawn by pipette, quenched in 100 ml. H_2O, acidified with 1 ml. concentrated H_2SO_4 and the residual H_2O_2 titrated with .1 N $KMNO_4$. The following table illustrates the results of the test.

Table 1

Stabilizing Agent [1], concentration (percent)	Time (min.)	Residual H_2O_2 (percent)
Control (no stabilizing agent)	15	0
0.001	20	98
	40	13
0.002	20	100
	40	91
0.01	20	100
	40	99
	60	98
	80	98
	180	93
	200	92
	240	50

[1] Amino tri(methylphosphonic acid).

As can be observed from the above table, a stabilizing agent of the instant invention is effective in stabilizing the peroxy solutions at very low concentrations (from .001% to .01%) over periods of time from about 20 minutes up to about 2 hours, while the peroxy solution without the stabilizing agent exhibited no bleaching ability after about 15 minutes.

In order to illustrate the bleaching ability of a peroxy solution stabilized with the compounds of the instant invention, the following tests were made with the indicated

results. Four 5" x 6" swatches of unbleached desized sheeting were prewet with distilled water and placed in a suitable stirrer flask containing 1 liter of a bleaching solution of the following initial composition: 0.35% H_2O_2, 1% sodium silicate, .25 p.p.m. Cu(II) (as $CuSO_4$) and stabilizing agent as indicated. The temperature was thermostated at about 90° C. At intervals of about 15 minutes, 10 ml. aliquots of solution were withdrawn by pipette and residual H_2O_2 determined by permanganate titration. Cloth swatches were withdrawn after 15, 30, 16 and 120 minutes; rinsed well in distilled water, and air dried. The swatches were pressed and then reflectance measured vs. the original unbleached cloth on a Gardner reflectometer. Averages of four readings at different cloth orientations are reported. Reflectance values for blue light were measured relative to a white ceramic plate as 100%. The test swatches were then cut into one inch strips and measured for tensile strength according to ASTM Designation D–39–49, revised 1955 "Standard General Methods of Testing Woven Fabrics," A Breaking Strength, 11. Raveled Strip method. The following tables illustrate the results of the test.

Table 2

Stabilizing Agent[1], concentration (percent)	Bleaching Times (min.)	Residual H_2O_2 (percent)	Reflectance (blue light) percent
0.01	0	100	69
	15	95	87
	30	94	90
	60	----------	92
	90	----------	93
0.1	0	100	69
	15	95	86
	30	92	88
	60	88	89
	90	86	91
	120	80	93

[1] Amino tri(methylphosphonic acid).

Table 3

Swatches bleached with stabilizing agent[1] in concentratiln as indicated (percent)	Bleaching Time (min.)	Breaking Strength (lbs.)
Control (unbleached)	----------	47.7
0.01	15	50
	30	50.8
	60	47.4
	120	46.5
0.1	15	45.8
	30	46.1
	60	46.5
	120	45.9

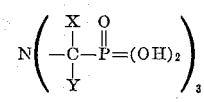
[1] Amino tri(methylphosphonic acid).

As can be observed from the above tables, the peroxy solutions stabilized with a compound of the instant invention exhibited the ability to raise the brightness of the bleached cotton fabric from about 69% (before the foregoing bleaching treatment) to about 86 to 93%. In addition, no substantial degradation of the fabric occurred as a result of bleaching with the stabilized peroxy solution as indicated in Table 5 with the tensile strengths of the bleached swatches comparing very favorably with the unbleached swatches. As can be appreciated, therefore, peroxy solutions stabilized with the stabilizing agents of the present invention exhibit the ability to bleach cellulosic materials, such as cotton fabric, without impairing the material.

While a peroxy solution in accordance with this invention need contain only a peroxy-compound and an amino tri(lower alkylidenephosphonic acid) or a salt thereof, it will be appreciated that the incorporation in the solution of additional ingredients commonly used in peroxy solutions, such as inorganic alkali metal basic materials, wetting agents, optical whiteners (brightening agents and fluorescent dyes) and the like, is contemplated as being within the invention.

What is claimed is:

1. A method for stabilizing peroxy solutions having concentrations of at least about 0.01 weight percent from decomposition which comprises dissolving therein in concentrations of at least about .001 weight percent a stabilizing agent selected from the group consisting of amino tri(lower alkylidenephosphonic) acids having the formula:



wherein X and Y are each selected from the group consisting of hydrogen and lower alkyl groups containing from 1 to 4 carbon atoms, and their water soluble salts selected from the group consisting of alkali metal salts, ammonium salts and amine salts.

2. The method of claim **1**, wherein said peroxy concentration is from about 0.01 to about 5 weight percent.

3. The method of claim **2**, wherein said stabilizing agent concentration is from about 0.001 to about 5 weight percent.

4. The method of claim 3, wherein said peroxy solution has a pH of from about 7.5 to about 12.5 and said stabilizing agent is an amino tri(lower alkylidene phosphonic acid).

5. The method of claim **4**, wherein said amino tri(lower alkylidene phosphonic acid) is amino tri(methyl phosphonic acid).

6. The method of claim **3**, wherein said peroxy solution has a pH of from about 7.5 to about 12.5 and said stabilizing agent is a water-soluble salt of an amino tri(lower alkylidene phosphonic acid).

7. The method of claim **6**, wherein the water-soluble salt of an amino tri(lower alkylidene phosphonic acid) is pentasodium amino tri(methyl phosphonate).

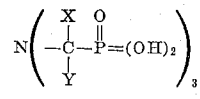
8. The method of claim **5**, wherein said peroxy solution is a solution of hydrogen peroxide.

9. The method of claim **7**, wherein said peroxy solution is a solution of hydrogen peroxide.

10. The method of claim **14**, wherein said peroxy solution is a solution of hydrogen peroxide.

11. The method of claim **16**, wherein said peroxy solution is a solution of hydrogen peroxide.

12. In the method for bleaching cellulosic material by contacting said material with a peroxy solution, the improvement which comprises carrying out said bleaching with said peroxy solution having concentrations of from about 0.01 to about 5 weight percent stabilized against decomposition by having dissolved therein in concentrations of from about 0.001 to about 5 weight percent a stabilizing agent selected from the group consisting of amino tri(lower alkylidenephosphonic) acids having the formula:



wherein X and Y are each selected from the group consisting of hydrogen and lower alkyl groups containing from 1 to 4 carbon atoms, and their water soluble salts selected from the group consisting of alkali metal salts, ammonium salts and amine salts.

13. The method of claim **12**, wherein said peroxy solution has a pH of from about 7.5 to about 12.5 and said stabilizing agent is an amino tri(lower alkylidene phosphonic acid).

14. The method of claim 13, wherein said amino tri-(lower alkylidene phosphonic acid) is amino tri(methyl phosphonic acid).

15. The method of claim 12, wherein said peroxy solution has a pH of from about 7.5 to about 12.5 and said stabilizing agent is a water-soluble salt of an amino tri-(lower alkylidene phosphonic acid).

16. The method of claim 15, wherein the water-soluble salt of an amino tri(lower alkylidene phosphonic acid) is pentasodium amino tri(methyl phosphonate).

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JULIUS GREENWALD, *Primary Examiner.*