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PROCESSES FOR STABILIZING PEROXY SOLUTIONS

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ABSTRACT OF THE DISCLOSURE

Alkaline aqueous solutions containing a peroxy compound and an alkali metal silicate are stabilized against substantial decomposition of said peroxy compound by the inclusion of a stabilizing agent which is, for example, a combination of nitrilotriacetic acid, 1-hydroxy ethylidene-1, 1-diphosphonic acid, and a magnesium or calcium salt, e.g., magnesium sulfate, and which stabilizing agent effects (1) reducing the decomposition of said peroxy compound and (2) preventing silicate deposition.

The present invention relates to an improved process for stabilizing peroxy solutions which are used for bleaching textile materials. Specifically, this invention is concerned with peroxy bleaching solutions which are aqueous alkaline solutions containing a peroxy compound, an alkali metal silicate and a novel combination which functions as a stabilizing agent for the reduction of the decomposition of the peroxy compound and prevention of silicate deposition.

Preparing textile materials for bleaching, dyeing and finishing generally involves a series of well-known steps. The material is first singed to burn off excess fibers, desized to remove any artificial coating put on the material for processing, rinsed, and then it is scoured. After scouring, the material is again rinsed and then, in succession, it is bleached, scoured, rinsed, mercerized, rinsed, dyed or printed, and finished. These steps are more specifically described in Chemistry and Chemical Technology of Cotton, Interscience Publishers, Inc., New York, N.Y., 1955, edited by Kyle Ward, Jr., and which is incorporated herein by reference. A discussion per se of the bleaching step starts on p. 190 of said publication.

In general, bleaching is the fifth major step in the above-described textile finishing process. The general purpose of the bleaching step is to oxidize any foreign matter on the textile material in order to provide a substantially absorbent and "white" material which is readily acceptive to dyeing.

The bleaching (oxidative) process is desirable in order to attempt to remove impurities or foreign matter and thus ultimately prepare a "whiteness in color" product suitable for subsequent dyeing and effecting a uniformity of color thereon. Generally, commercial bleaching (including boiling) processes involve contacting the textile material with alkaline aqueous solution (bath) containing a peroxy compound such as hydrogen peroxide and an alkali metal silicate such as sodium silicate.

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 (bleaching) 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 conditions 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 a stabilizing agent which affects synergism in the reduction of the decomposition of the peroxy compound and also prevents water-insoluble silicate deposition.

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 in view of the subsequent detailed description and appended claims.

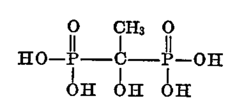
It has been unexpectedly found that the above objects can be accomplished by including a synergistic stabilizing agent which is a combination of:

(1) Nitrilotriacetic acid (NTA)

$$N(CH_2COOH)_3$$

and water soluble salts thereof;

(2) 1 - dhydroxy ethylidene - 1,1 - diphosphonic acid (HEDP)



and water soluble salts thereof; and

(3) A water soluble magnesium or calcium salt in the aqueous peroxy solution.

It is to be understood in conjunction with NTA and HEDP acids per se, the water-soluble salts are also included within the scope of the present invention. The preferred salts are the sodium salts. 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, which exhibit the characteristics of the alkali metal salt may also be used to practice the invention.

The magnesium and calcium salts include, without limitation, magnesium acetate, magnesium benzoate, magnesium bromate, magnesium bromide, magnesium chlorate, magnesium chloride, magnesium chromate, magnesium citrate, magnesium fluosilicate, magnesium formate, magnesium lactate, magnesium nitrate, magnesium nitrite, magnesium hypophosphate, magnesium selenate, magnesium sulfate, magnesium sulfite, magnesium thiosulfate, calcium butyrate, calcium chlorate, calcium chloride, calcium hypochlorite, calcium chromate, calcium formate, calcium gluconate, calcium lactate, calcium maleate, calcium nitrate, calcium nitrite, calcium propionate, calcium 1-quinate, calcium sulfide, calcium dithionate, calcium thiosulfate, calcium valerate, and mixtures of these salts. The above list is not all inclusive and the magnesium or calcium salt is anyone which is water-soluble and provides magnesium or calcium ions in aqueous system. It is to be noted that these salts include both inorganic and organic salts.

It is to be understood that the magnesium or calcium salt can be supplied to the aqueous peroxy solution in the form of the magnesium or calcium salts of NTA and/or HEDP. In other words, the novel stabilizing agent can be in the form of (1) a three-component combination of NTA, HEDP, and a magnesium or calcium salt (such as magnesium sulfate), or (2) a two-component combination of the magnesium or calcium salts of NTA and HEDP.

It is desirable that the mole ratios of NTA:Mg or Ca salt:HEDP be in the range of from about 1:1:1 to about 5:3:1, preferably from about 2:1:1 to about 2:2:1.

It is to be understood that the term "textile" material as used herein includes any natural and/or synthetic fibrous base material such as cotton, nylon, viscose rayon, polyester, e.g., Dacron, hemp, linen, jute, and blends thereof such as, for example, cotton-Dacron, cotton-Dacron-viscose rayon, cotton-nylon-viscose rayon, cotton-Dacron-nylon, cotton-nylon, and cotton-polyester (all in various weight rations).

If one so desires to use a surfactant in the peroxy (bleaching) solution, the specific synthetic organic surfactant can be any of a wide variety of surface active agents. Typical surfactants are described in U.S. Pats. 2,846,398 and 3,159,581, both of which are incorporated herein by reference. Furthermore, other publications which describe surfactants which can be used in the present invention processes include Schwartz and Perry, "Surface Active Agents," Interscience Publishers, New York (1949) and "The Journal of American Oil Chemists Society," vol. 34, No. 4, pp. 170–216 (April 1957), both of which publications are incorporated herein by reference. The amount of surfactant will vary, depending upon various process conditions and any amount can be used as long as no substantial adverse effect is incurred in the bleaching operation.

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, inter alia, the particular peroxycompound used, the pH of the aqueous peroxy solution is usually adjusted with any caustic material in order to effect a pH of greater than 7, e.g. 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 7.0, the rate of bleaching in most cases is slow to the extent of being uneconomical for bleaching. In general, the amounts of caustic used are from about 1% to about 4% by weight based on the total weight of the alkaline aqueous (peroxy) solution.

The concentration of peroxy 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. It is to be understood that the concentration is not a limitation herein and that any

concenration can be utilized as long as the desired end result is achieved.

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 concentated 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, interalia, 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 textile material by immerision 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 textile material by saturation, removing he excess moisture and exposing the textile 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. Pats. 2,839,353, 2,960,-383, and 2,983,568 are illustrative of being representative of continuous peroxy bleaching methods.

Additional publications which relates to peroxy bleaching and/or bleaching of textile materials include, without limitation, U.S. Pats. 2,493,740; 2,515,532; 2,524,-113; 2,602,723; 2,686,104; 2,718,528; 2,740,689; 2,803,-517; 2,820,690; 2,839,353; 2,858,184; 2,868,615; 2,893-814; 2,893,819; 2,917,528; 2,927,082; 2,927,840; 2,950,-175; 2,960,383; 2,970,882; 2,983,568; 2,991,168; 3,003,-910; 3,043,645; 3,053,634; 3,089,753; 3,122,417; 3,156,-654; 3,211,658; 3,234,140; 3,243,378; 3,278,445, and 3,383,174; Belgium Pat. 661,582; British Pats. 793,733; 852,102, and 866,764; French Pats. 1,420,462, and 1,999,-350; German Pat. 1,027,174; Japanese Pats. 9600 ('57), and 238 ('58); Netherlands Pat. 6515967; and "Preparation and Bleaching," Textile World Refresher, by K. S. Campbell, 1961, McGraw-Hill Publishing Co., New York. All of these publications are to be considered as incorporated herein by reference.

The temperature of the bleaching (peroxy) solution is desirable in the range of from about 72° F. to the boiling point of the bleaching solution but temperatures from about 140–210° F. are preferred. It is to be understood that higher temperatures, such as 250° F. to 300° F., can be used (with the aid of superatmospheric pressure) where one so desires.

The practice of the invention and the advantages provided thereby are further illustrated by the following examples which are not intended to be limitative:

EXAMPLE I

In order to illustrate the stabilizing ability of the stabilizing agents of the present invention, the following test is conducted with the indicated results.

The bleaching solutions shown in Table I are prepared by mixing together 900 milliliters of deionized water, 22 grams of hydrogen peroxide (35% aqueous solution), 11 grams of sodium silicate, 5 grams of sodium hydroxide (50% aqueous solution) and the indicated amount of the stabilizing agent. Ferrous sulfate is added to the resulting solution in an amount to provide 2 parts per million (p.p.m.) of Fe^{++} therein.

Each individual bleaching solution is contained in a suitable Pyrex glass beaker which in turn is in a thermostated bath of the Ahiba laboratory dyeing machine. Each bleaching solution is heated to and maintained at 210° F. for a period of 120 minutes. At the intervals so indicated in Table I, 10 milliliters (ml.) aliquots of solution are withdrawn by pipette, quenched in 100 ml. of H_2O, acidified with 1 ml. concentrated H_2SO_4 and the residual H_2O_2 is titrated with 0.1 N KM_nO_4. The percent available oxygen (remaining in the bleaching solution at that particular time) is calculated as follows:

$$\text{Percent available } O_2 = \frac{(\text{mls. } Km_nO_4)\ (\text{normality of } Km_nO_4)\ (0.008)\ 100}{\text{weight of original } H_2O \text{ in solution}}$$

The results of this test are shown in Table I.

It is believed that the addition of a salt of calcium and/or magnesium to a solution of a soluble silicate results in a formation of an insoluble metal silicate. For example, it is believed that the reaction occurs between the polysilicic acid through the silanol group and a basic metal ion like $Fe(OH)_2$ as follows:

$$\cdot SiOH + Fe(OH)_2 \rightarrow (\cdot SiOFeOH)^+$$

While the iron in this form might still act as a catalyst in peroxy compound decomposition, it is believed that the presence of Mg^{++} and/or Ca^{++} in the peroxy/silicate solution leads to the formation of an extensive network of Mg and/or Ca silicates which form a protective colloidal coat over the heavy metal-silicic acid complex, and thus immobilizes the heavy metal as a catalyst.

It is believed that in the case of the present invention stabilizing agent, i.e., the combination of NTA, Mg and/or Ca salt and HEDP, the Mg and/or Ca silicate complex does the stabilizing of the peroxy compound rather than NTA and/or HEDP. Thus, it is believed that HEDP and NTA serve as a "carrier" for the Mg and/or Ca and when combined as a sequestrant for excessive hardness in bleaching solutions to prevent insoluble silicate precipitates which would adversely effect the overall textile treating process. Experimentation has shown that this combination of NTA and HEDP is exceptionally unique and results in unexpected results when used in combination with a Mg and/or Ca salt. The addition of Mg and/or Ca salts, without NTA and/or HEDP, stabilizes peroxy bleaching solutions to a minor degree; however, their use is quite limited because they have poor solubility and promote insoluble silicate precipitates if used in the absence of HEDP and NTA.

The above beliefs are merely ideas as to how possibly the stabilizing agent of the present invention functions in a peroxy-silicate bleaching solution. These ideas are not to be considered as limitations in any manner whatsoever in the present invention.

TABLE I

Effect of stabilizing agents on peroxide bleach stability in deionized water in the presence of 2 p.p.m. Fe^{++}, 22 g./l. H_2O_2, 35%; 11 g./l. sodium silicate,[1] 5 g./l. NaOH, 50%,[1] pH 11.3 at 210° F.

Stabilizing agent	No stabilizing agent	HEDP,[2] 2 g./l.	ATMP,[3] 2 g./l.	HEDTA,[4] 2 g./l.	NTA,[5] 2 g./l.	Present invention,[6] 2 g./l.
Percent available oxygen remaining in bleach solution after—						
5 minutes	84	85	97	80	83	98
15 minutes	7	52	92	4	35	94
30 minutes	0	1	4	0	0	84
60 minutes	0	0	0	0	0	75
120 minutes	0	0	0	0	0	65

[1] Low amounts of sodium silicate and high pH contribute to peroxide instability.
[2] Disodium salt of 1-hydroxy ethylidene-1, 1-diphosphonic acid.
[3] Tetra sodium salt of amino tri(methylene phosphonic acid)—40% solids; note U.S. 3,234,140.
[4] Hydroxy ethylene trisodium acetate, 40% solids; prior art.
[5] Trisodium salt of nitrilo triacetic acid.
[6] 36.1% solution of 1 mole NTA/0.47 mole Mg (from $MgSO_4$)/0.3 mole HEDP.

It is to be noted in Table I, that in addition to the present invention stabilizing agent, other materials are shown for comparative purposes. Table I readily shows that the sodium salts of NTA and HEDP are poor stabilizing agents as compared to the present invention stabilizing agent (shown in Table I) of the combination of NTA, Mg^{++} and HEDP. ATMP is representative of the prior art—U.S. Pat. 3,234,140.

EXAMPLE II

Example I above is repeated in toto with the sole exception that in place of the 2 p.p.m. Fe^{++} in the bleaching solution, 2 p.p.m. of Cu^{++} is present. Substantially the same results are obtained as that shown in Table I.

EXAMPLE III

Example I above is repeated in toto with the sole exception that in place of the 2 p.p.m. Fe^{++} in the bleaching solution, there is present in the solution, by addition of a corresponding water-soluble salt, 0.85 p.p.m. Fe^{++}, 0.17 p.p.m. Cu^{++}, 0.40 Zn^{++} and 0.10 Pb^{++}. Substantially the same results are obtained as that shown in Table I.

EXAMPLE IV

The exact mechanism of how the novel combination of NTA, HEDP and a water-soluble magnesium and/or calcium salt effectively act as a stabilizing agent is not known. Table I shows, however, that NTA per se and HEDP per se are poor stabilizing agents in an aqueous alkaline bleaching solution containing a peroxy compound and an alkali metal silicate and catalytically-active substances such as iron, copper, manganese which greatly accelerate the decomposition of the peroxy-compound.

TABLE II

Effect of additives on the formation of Ca and Mg silicate precipitates in hydrogen peroxide/sodium silicate bleach solutions [1]

	Grams per liter			
	40% solution of—			
	$NTA \cdot 3Na \cdot H_2O$	$NTA \cdot 3Na \cdot H_2O$ plus ½ mole Mg/mole NTA	HEDP	Hours during which H_2O_2 silicate solutions remained free of precipitates (clear)
1				0
2	1.0			0
3	2.0			2½
4		1.0		0
5		2.0		2½
6		1.0	0.25	12
7		1.0	0.50	24
8		2.0	0.125	4
9		2.0	0.25	12
10		2.0	0.50	24
11		4.0	0.25	6
12		4.0	0.50	12

[1] 22 g./l. H_2O_2 35%. 22 g./l. sodium silicate. 0.25 p.p.m. Cu^{++}, 400 p.p.m. as $CaCO_3$ from 2Ca:1Mg (from $CaCl_2$ and $MgSO_4$).

In order to demonstrate the effect of NTA, HEDP, Ca and Mg alone or in combination regarding silicate precipitation, eleven bleaching solutions (designated solutions 2–12 in Table II) are prepared in the same manner as set forth in Example I. Solution No. 1 is a blank with no additives and is used as a control. Solutions designated Nos. 6–12 are representative of the present invention.

Table II readily shows that NTA per se and a Mg salt+NTA combination (representative of the prior art) are quite inferior if not completely ineffective in preventing silicate precipitation in bleaching solutions as compared to the novel combination of NTA, HEDP and a Mg and/or Ca salt.

In view of the results set forth in Examples I–IV, it is seen that two conditions must be concurrently satisfied in order to obtain effective bleaching with an aqueous alkaline solution containing a peroxy compound and an alkali metal silicate, i.e., (1) the peroxy compound must not be substantially decomposed over a relatively short period of time, e.g., 1 to 2 hours and (2) the silicates in solution must remain in solution and not substantially precipitate out over a relative period of time. Both of these conditions are satisfied by the stabilizing agent of the present invention, but not by the individual components thereof or by the Mg salt+NTA combination.

EXAMPLE V

In order to illustrate the bleaching ability of a peroxy solution stabilized with the present invention stabilizing agents (and prior art materials for comparative purposes), the following tests are made with the indicated results set forth in Table III. Several sets of four 5″ x 6″ swatches of unbleached desized sheeting are prewet with distilled water and each set is placed in a suitable stirrer flask containing 1 liter of a bleaching solution of the following initial composition: 22 grams of a 35% H_2O_2 solution, 11 grams of sodium silicate, 5 grams of a 50% NaOH solution, 0.85 p.p.m. Fe^{++}, 0.17 p.p.m. Cu, 0.40 p.p.m. Zn^{++}, 0.10 p.p.m. Pb and the stabilizing agent as indicated in Table III. The temperature was thermostated at about 210° F. At intervals of about 15 minutes, 10 ml. aliquots of solution are withdrawn by pipette and residual H_2O_2 determined by permanganate titration as described in Example I above. The cloth swatches are withdrawn after 15, 30, 60 and 120 minutes; rinsed well (twice) in distilled water at 210° F., and air dried. The swatches are pressed and then reflectance measured vs. the original unbleached cloth. Averages of four readings at different cloth orientations are reported. The degree of bleaching is set forth in terms of "fabric whiteness" as determined by a Gardner Automatic Color Difference Meter made by Gardner Laboratory, Inc., Bethesda, Md. The "fabric whiteness" numbers shown in Table III are determined relative to a standard (MgO filter being equal to 100) which was as close to perfect whiteness as is possible. The results of this Example V are set forth in Table III. Regarding these "whiteness" numbers, a difference of one (1) unit is considered significant.

TABLE III

Effect of stabilizing agents on peroxide bleach stability and on bleaching of cotton fabric[1] in deionized water in the presence of several heavy metals[2] and at pH 11.3[3]

	Stabilizing agent					
	None (control)	ATMP, 4.23 g./l.	DEPTA plus $CaCl_2$,[4] 4.23 g./l.	DEPTA plus $CaCl_2$,[4] 4.23 g./l.	Present invention[6] 4.23 g./l.	Present invention[6] 1.75 g./l.
Fabric whiteness number	66	87	85	86	92	92
Percent available oxygen remaining in bleach solutions after—						
5 minutes	[7] 61	89	78	77	98	99
15 minutes		51	10	17	88	85
30 minutes	3	6	1	4	77	65
45 minutes	0	2	0	1	68	52
60 minutes		0.5		0	59	40

[1] 100% cotton fabric, desized and scoured in a textile mill.
[2] P.p.m.: Fe, 0.85; Cu, 0.17; Zn, 0.40; Pb, 0.10.
[3] Low amounts of sodium silicate and high pH contribute to peroxide instability.
[4] Diethylene triamine pentasodium acetate plus $CaCl_2$, 24.85% solids.
[5] Diethylene triamine pentasodium acetate plus $CaCl_2$, 32% solids.
[6] 36.1% solution of 1 mole NTA/0.47 mole Mg/0.3 mole HEDP.
[7] This solution is extremely unstable and cannot be heated up to 210° F. These values are obtained after heating to 60° C. This solution is not used for bleaching of fabric sample.

In conjunction with Table III, it is vividly demonstrated that the stabilizing agents of the present invention exhibit an unexpected result and are substantially better than the prior art materials such as ATMP. Specifically, it can be seen that with no stabilizing agent in the bleaching solution, the fabric had a whiteness number of 66; with ATMP the value was 87 and with DETPA+$CaCl_2$, the value was 85 and 86. But with the novel stabilizing agents of the present invention, the average value was 92, a significant difference and improvement. The superiority of these novel stabilizing agents is thus seen.

The test swatches bleached with the solution containing the present invention stabilizing agents are 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. No substantial degradation of the fabric occurred as a result of bleaching with the stabilized peroxy solution, i.e., the tensile strengths of the bleached swatches compared very favorably with unbleached swatches which are similarly tested. Consequently, 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, an alkali metal silicate and the novel stabilizing agents, 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.

The foregoing examples have been described in this specification for the purpose of illustration and not limitation. Many other modifications and ramifications will naturally suggest themselves to those skilled in the art based on this disclosure. These are intended to be comprehended as within the scope of this invention.

In view of the aforegoing subject matter and particularly the examples, it is to be expressly understood that the novel combination of NTA, HEDP and a water-soluble magnesium or calcium salt (e.g., magnesium sulfate) functions in two different aspects: (1) reduction of the decomposition of the peroxy compound and (2) prevention of the precipitation of water-insoluble silicates. Thus, the term "stabilizer" as used herein is intended to encompass both of these aspects. The novelty of this unique combination is predicated upon these two aspects (although the exact physical and/or chemical mechanism is not known) and as such constitutes a significant advancement in the art.

What is claimed is:

1. A method for stabilizing aqueous alkaline solutions of peroxy compounds from decomposition of said peroxy compounds which comprises dissolving in said solution a stabilizing agent which is a combination of (a) 1-hydroxy ethylidene-1,1-diphosphonic acid and the water-soluble salts thereof; (b) a water-soluble salt of magnesium or calcium and (c) nitrilotriacetic acid and water-soluble salts thereof, the mole ratio of (a):(b):(c) being from about 1:1:1 to about 1:3:5, and the concentration of said stabilizing agent in said solution being from about 0.001 to about 5 percent by weight.

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

3. The method of claim **2**, wherein said solution has a pH of from about 7.0 to about 12.5 and said stabilizing agent contains a water-soluble magnesium salt.

4. The method of claim **3**, wherein said magnesium salt is magnesium sulfate.

5. The method of claim **3**, wherein said solution has a pH of from about 7.0 to about 12.5 and said stabilizing agent consists of (a) 1-hydroxy ethylidene-1,1-diphosphonic acid; (b) a water-soluble magnesium salt; and (c) nitrilotriacetic acid in a mole ratio respectively of from about 1:1:1 to about 1:3:5.

6. The method of claim **5**, wherein the water-soluble magnesium salt is magnesium sulfate.

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8—111; 252—95, 99