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2,927,082

PEROXIDE BLEACHING COMPOSITIONS
AND THEIR USE

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No Drawing. Application January 19, 1956
Serial No. 560,063

7 Claims. (Cl. 252-186)

This invention relates to improved peroxide bleaching compositions and to their use, particularly in bleaching cellulosic materials, whether natural or regenerated. More particularly, it relates to improved peroxide bleaching compositions of relatively high alkalinity and to their use in bleaching cellulosic materials such as cotton goods, wood pulps, and the like.

Alkaline peroxide bleaching solutions must generally be stabilized to prevent excessive decomposition of the peroxide since such decomposition is wasteful, results in poor bleaching, and may cause damage to the goods being bleached. The usual stabilizer is sodium silicate, with or without small amounts of magnesium compounds. Other stabilizers such as phosphates are sometimes used.

While silicate stabilizers are cheap and usually effective, their use is frequently objectionable. Silicates generally leave deposits on equipment surfaces requiring periodic shut downs for their removal. Such deposits formed on cloth prevent even dyeing and when formed on paper may interfere with printing. A further disadvantage is that silicates are poor stabilizers at alkalinities substantially above pH 11. Magnesium compounds when used as stabilizers cause precipitation of insoluble compounds such as magnesium hydroxide, resulting in a non-uniform effect, especially at alkalinities above about pH 11.5.

There are a number of instances where bleaching at alkalinities of at least pH 11.5 would be desirable. Thus, cotton is bleached faster at such high alkalinities, mores are more easily removed, and some combinations of cotton and synthetic fabrics respond more favorably to bleaching under such conditions.

It is an object of the invention to provide improved alkaline peroxide bleaching compositions. A further object is to provide an improved stabilizer combination especially adapted for use in peroxide bleaching compositions of relatively high alkalinities. Another object is to provide an improved bleaching method, particularly for bleaching cellulose, employing such improved bleaching compositions. Still further objects will be apparent from the following description.

The objects of the invention are accomplished (1) by the preparation of alkaline peroxide bleaching compositions containing as a stabilizer a magnesium-gluconate chelate, particularly compositions having a pH of at least 11, (2) by the compositions so prepared, and (3) by the use of such compositions in bleaching materials, particularly cellulose.

It has been discovered that a water-soluble gluconate such as the alkali metal gluconates, or a precursor thereof (such as gluconic acid or its lactone) which yields a soluble gluconate in an aqueous alkaline peroxide solution, chelates the magnesium ion and prevents or delays precipitation of insoluble magnesium compounds such as magnesium hydroxide in the present compositions, and that the resulting magnesium-gluconate chelate is an effective stabilizer for alkaline peroxide solutions. Such a chelate provides effective stabilization over a wide pH

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range and is particularly useful at a pH range of about 11 to 14. It can be employed at lower and higher alkalinities either alone or in combination with other stabilizers, e.g., silicate, but its use will be most valuable at pH values in the range 11 to 14 since previously employed stabilizers are ineffective or relatively so in this range, or cause undesirable precipitation when used.

The invention is illustrated by the following examples in which all percentages of reagents are based upon the solution weights and all reflectance values were determined on a Hunter multi-purpose reflectometer and represent percent reflectances based on the reflectance from magnesium carbonate at 100%.

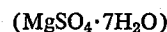
EXAMPLE 1

Bleach solution A

An aqueous bleach solution was prepared containing 0.4% hydrogen peroxide (H_2O_2) and 1.5% of a 42° Bé. sodium silicate solution (approximate composition: 10% Na_2O , 25% SiO_2 and 65% H_2O). Sodium hydroxide was added as required to three samples of the solution to adjust the pH thereof to the values shown in the table below.

Bleach solution B

An aqueous bleach solution was prepared containing 0.4% hydrogen peroxide (H_2O_2), 0.3% gluconic acid (or glucono lactone) and 0.1% Epsom salt



Sodium hydroxide was added as required to three samples of the solution to adjust the pH thereof to the values shown in the table below.

The above samples of Bleach solutions A and B were analyzed for active oxygen, heated for 30 minutes at 100° C. and again analyzed to determine the active oxygen lost during the heating period. Results were:

Solution	pH	Percent of Orig. Active Oxygen Lost
A.....	10.2	13
A.....	11.0	18
A.....	12.0	40
B.....	11.0	10
B.....	11.5	12
B.....	12.2	16

These results show that the magnesium-gluconate combination is substantially more effective as a stabilizer than is sodium silicate at a pH of 11 or higher and is outstandingly more effective at a pH of about 12.

EXAMPLE 2

An aqueous solution (A) was prepared containing 0.1% Epsom salt and 0.4% hydrogen peroxide (H_2O_2). A similar solution (B) was prepared containing 0.3% glucono lactone in place of the Epsom salt. Each solution was adjusted to a pH of 12.2 by the addition of sodium hydroxide. The solutions were analyzed for their active oxygen contents, heated at 100° C. for 30 minutes, then reanalyzed to determined active oxygen losses. Solution A lost 96% of its active oxygen while solution B lost 99%. These results show that neither Epsom salt nor sodium gluconate is an effective stabilizer when used alone at this high alkalinity.

EXAMPLE 3

Samples of an unbleached muslin cloth were rinsed in a 0.5% solution of Epsom salt, then immersed in portions of Bleach solutions A or B of Example 1 whose alkalinities had been adjusted to the pH values shown in the table below by the addition of sodium hydroxide.

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The bleach solutions with the cloth samples were then heated for 15 minutes at 100° C. From analyses of the solutions before and after the heating period, the active oxygen losses shown in the following table were found.

Solution	pH	Percent of Orig. Active Oxygen Lost
A.....	10.4	15.0
A.....	11.5	46.0
B.....	11.2	12.0
B.....	11.7	9.0

These results show that the stabilizing effectiveness of the magnesium-gluconate combination is superior to silicate at a pH of about 11.5 under bleaching conditions in the presence of muslin.

EXAMPLE 4

Samples of unbleached muslin cloth of about 58% reflectance were rinsed in water alone or in a 0.5% solution of Epsom salt, then bleached for 15 minutes at 100° C. in portions of Bleach solution A or B of Example 1 at the pH values (derived by the addition of sodium hydroxide as required) indicated in the following table.

Pre-Rinse	Bleach Solution		Percent Reflectance After Bleaching
	A or B	pH	
Water.....	A	12.0	81.7
ESS ¹	A	12.0	83.3
Water.....	B	12.2	84.1
ESS ¹	B	12.2	85.0

¹ 0.5% Epsom salt solution.

These results show that at about pH 12 substantially better bleaching results using the present stabilizer than when using silicate or silicate in combination with magnesium sulfate.

Tests have shown that cotton fabric bleached using the present bleaching compositions at high alkalinities compares favorably respecting properties such as absorbency and extent of degradation with fabric bleached using silicate bleaching compositions at lower alkalinities. Bleaching by the present method can be preceded by any of the conventional pretreatments, such as wetting out treatment, a desizing treatment, an alkaline or acidic scouring treatment, a reducing treatment, or a combination of one or more such treatments.

Any magnesium compound such as the sulfate, acetate and nitrate, which is normally soluble in water can be used for the present purpose. The preferred compound is magnesium sulfate which is available commercially as Epsom salt. Concentrations of the magnesium compound of at least 0.03%, and preferably 0.08 to 0.5%, will generally be used. Higher concentrations are also effective but usually offer no added advantage. The magnesium compound can be added directly to the bleach solution, or part or all may be added to the cellulosic material as a pretreatment.

The gluconate, gluconic acid or glucono lactone should be added to the bleach solution in an amount sufficient to chelate all or a substantial part of the magnesium compound employed. Addition of any small amount of a gluconate, or a gluconate precursor, will have a beneficial effect but generally at least one mole, preferably 2 to 4 moles, thereof per mole of the magnesium compound will be used.

The concentration of hydrogen peroxide, or equivalent peroxygen compound such as sodium peroxide or sodium perborate, in the bleach solution can be varied considerably depending upon the results desired. Generally it will range from about 0.5% to 2.0% (as H₂O₂) or

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higher. Concentrations of 0.4 to 1.0% are satisfactory for most purposes.

Any soluble strong alkali, preferably an alkali metal hydroxide or peroxide, can be employed, if necessary, to increase the alkalinity of the bleach solution to a pH value of at least 11.0, e.g. 11 to 14, preferably 11.5 to 13, when such high alkalinities are desired. Higher alkalinities can also be employed. When employing sodium peroxide, it can supply part or all of both the active oxygen and alkali requirements.

Bleaching using the present compositions can be carried out over a wide range of temperature. At low temperature such as 30 to 50° C. the bleaching time will usually range from 8 to about 24 hours. At around 100° C., a time of 15 to 60 minutes is generally satisfactory while times as short as 2 minutes to 30 seconds may be sufficient at temperatures of 110 to 150° C. (under pressure).

Any cellulosic material which responds favorably to bleaching with alkaline peroxide can be bleached by the present method. Examples are cotton textile goods, wood pulps and fabrics which are blends of cotton and nylon fibers.

The chelating effect of gluconates upon magnesium ion at the present high alkalinities appears to be unique since polyphosphates, citric acid and tartaric acid were found to be substantially ineffective for this purpose and their combinations with magnesium compounds were not effective stabilizers at the present high alkalinities.

I claim:

1. A bleaching composition comprising an aqueous hydrogen peroxide solution having a pH of 11 to 14 and containing, based upon the weight of said solution, 0.05 to 2% H₂O₂ and a stabilizer combination of (a) 0.03 to 0.05% of water-soluble magnesium salt and (b) from 1 to 4 moles, per mole of said magnesium salt, of a compound of the group consisting of gluconic acid, glucono lactone and the alkali metal gluconates.

2. A composition according to claim 1 having a pH of 11.5 to 13.

3. A composition according to claim 1 wherein the magnesium salt is Epsom salt.

4. The method of bleaching cellulose comprising subjecting said cellulose to the action of a bleaching composition as defined in claim 1.

5. The method of bleaching a cotton textile material comprising subjecting said textile material to the action of a bleaching composition as defined in claim 1.

6. The method of bleaching cellulose comprising subjecting said cellulose to the action of a bleaching composition as defined in claim 2.

7. The method of bleaching cellulose comprising subjecting said cellulose to the action of a bleaching composition as defined in claim 3.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,927,082

March 1, 1960

James H. Young

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 13, for "at" read -- as --; column 3, line 4, for "as wetting" read -- as a wetting --; line 73, for "0.5%" re -- 0.05% --; column 4, line 37, for "flucono" read -- glucono--.

Signed and sealed this 9th day of August 1960.

(SEAL)

Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents

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