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(54) **Stable concentrated hydrogen peroxide compositions for bleaching textiles**

(57) The present invention relates to a bleaching composition for use in industrial scale bleaching processes. The composition comprises alkaline peroxides and phosphonic acid derivatives that stabilize the peroxides for long periods and harsh conditions of environment, and optionally auxiliary ingredients such as surfactants and wetting agents. The invention also pertains to a process for treating textile materials involving the composition of the invention and a textile article treated according to such process.

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Description

Field of the Invention

[0001] The present invention relates to a bleaching composition designed for industrial use in treating textile articles. More specifically, the invention is pertaining to a stable composition having high peroxide content, wherein the stability problems related with high peroxide concentration are eliminated by phosphonic acid derivatives of the present invention.

Background of the Invention

[0002] Among the conventional bleaching agents such as hypochlorites, peroxides, various acids and chlorites, peroxide compounds *inter alia* are becoming the most prominent agents for bleaching purposes in the textile industry because of their high efficiency and environment friendly structure releasing only oxygen and water upon degradation. While peroxide bleaching has considerable advantages over alternative bleaching agents, they still have limitations in storage and use as their stability is prone to diminish by the effect of external and internal conditions such as heat, light, water, alkaline reagents, metals and certain impurities that may cause rapid degradation. Trace amounts of transition metals such as iron and copper promote catalytic decomposition of hydrogen peroxide leading to loss of peroxide from the bleaching solution. This has certain consequences as for example inferior bleaching quality and loss of textile material at the end of the bleaching process. Thereby, the operators are forced to use more chemicals or take certain measures as summarized below.

[0003] The bath liquor of a bleaching process is generally added a bleaching agent (i.e. peroxides), an alkaline substance, and further auxiliary chemicals such as wetting agents, oil removers, surfactants, sequestrants and stabilizers. One of the conventional techniques to eliminate the aforementioned problems is generally carried out by dosing of the peroxide and auxiliary agents separately to the bath liquor in order to prevent degradation of the peroxides prior to textile treatment procedure. This technique, however fails to prevent the bleaching agents to get into degradation because the peroxides come into contact with degradation promoting substances before meeting with the stabilizers. Correct and timely dosing of the chemicals does not facilitate to solve this problem.

[0004] Various attempts have also been made to provide an easily applicable bleaching bath by combining the auxiliary reagents as mentioned above into a single composition. However, combining of peroxides with said auxiliaries did not result in a satisfactory solution for textile treatment because the high concentrations of peroxides (i.e. 25-50% wt) in the industrial scale are tend to drive into degradation with small amounts of impurities.

[0005] To alleviate these problems, stabilizers have been focus of those skilled in the art having the objective of combining major ingredients of a bleaching bath into a ready to use composition. GB 1 385 885, for instance proposes aminocarboxylic acids and alkali metal salts thereof as organic sequestrants for stabilizing hydrogen peroxide wherein the amount of hydrogen peroxide is limited to a range between 0.2 and 1.8%. Similarly, US 5 482 516 discloses magnesium salts, particularly a mixture of MgO and citric acid as stabilizing agents.

[0006] To provide more effective stabilizers, various phosphate derivatives have also been known in the technical field as for instance disclosed in WO 97/48785, wherein the concentration of the peroxide is limited to a maximum value of 15% wt. These and other references of prior art using of certain stabilizers, although providing effective stabilization and metal ion complexing performance in bleach compositions mainly for household purposes, are not suitable to be used in industrial scale bleaching compositions wherein the peroxide concentrations are rather high, i.e. ranging from 25 to 50% wt.

[0007] Another solution for compensation of the loss of activity of peroxides is provided by use of peroxide or peroxide releasable compounds along with a bleach activator that activates the peroxy groups as disclosed for instance in EP 0 667 392. These compositions, however do not ensure satisfactory stability and neither have they solved the aforementioned problems with a cost effective way as they need extra activators.

[0008] As summarized above, the prior art compositions are mainly aiming at solving the stability problems of peroxides when concentration thereof is generally less than 10%. These compositions are mainly designed for household applications rather than the industrial scale requiring high concentrations of peroxides. The prior art references, on the other hand, do not provide an industrial bleaching agent that is capable of functioning at low temperatures thanks to the highly stabilized peroxides inside the composition.

[0009] It is therefore one of the objects of the present invention to provide a bleaching composition that remains stable for long storage periods even when the peroxide concentration is rather high in the level of 25-50% wt.

[0010] A further object of the present invention is to provide highly concentrated bleaching compositions that are suitable to function at lower temperatures as compared to the conventional bleaching compositions.

[0011] Another object of the present invention is to provide a textile bleaching process involving the bleaching compositions of the present invention.

[0012] Still a further object of the present invention is to provide a novel textile article that is efficiently bleached

according to the present invention.

[0013] These and other objectives of the present invention are solved by a composition, process and novel textile article as defined in the independent claims.

Summary of the Invention

[0014] The present invention relates to a bleaching composition for use in industrial scale bleaching processes wherein the peroxide concentrations exceed the values over 25% wt. To provide effective stabilization of these peroxides, there is proposed phosphonic acid derivatives that are mainly consisting of amino alkyl phosphonic acids such as amino-trimethyl phosphonic acid, hydroxy-ethyl diphosphonic acid and diethylene triamin-pentaphosphonic acid. A further surprising effect of the present invention appears when modified phosphonates, i.e. N-oxide alkaline salts of phosphonates are used along with the aforementioned phosphonic acid compounds in the bleaching composition.

[0015] The composition according to the present invention may further comprise auxiliary ingredients such as wetting and surface active agents. According to a further aspect, a process for treating textile articles in a bleaching liquor involving the composition of the present invention is provided. In another aspect, novel textile articles treated with the aforementioned process is disclosed, wherein said textile articles exhibit less deformation and loss of textile material, and also less amount of stains caused by metal salts of the bath liquor.

Detailed Description of the Invention

[0016] According to a first aspect of the present invention, there is provided an aqueous bleaching composition having combined character along with auxiliary chemicals and having stabilized nature with high resistance to light, water, impurities and metal ions that cause rapid degradation and loss of activity. Peroxide composition of the invention is thereby providing long periods of storage without losing its activity, and an efficient bleaching process with better performance of bleaching activity which also considerably diminishes loss of textile fibers at the end of the overall process.

[0017] In textile industry, bleaching compositions having peroxide concentrations of over 25% wt are classified as industrial scale compositions that need special handling and storage because of higher risk of degradation. According to the first aspect, the bleaching composition of the invention is designed for industrial use with a peroxide content of more than 25% wt, preferably more than 30% wt, more preferably between 25 and 50% wt, and most preferably between 30 and 40% wt.

[0018] As conventionally known from the textile treatment technology, bleaching processes are carried out in alkaline conditions at a pH value around 10-11. The alkalinity can be provided with any basic agent such as hydroxides of alkali metals as conventionally applied in the field. Thus, the composition of the present invention is suitable to be used with a conventional base in a bleaching process. Accordingly, such basic material and composition of the present invention can be separately dosed to a bleaching bath liquor.

[0019] According to the aforementioned first aspect, the composition of the present invention further comprises stabilizers and sequestrants that are found to be surprisingly effective in keeping the peroxides stable over extended periods of their shelf life. Said stabilizers are selected from the group of amino alkyl phosphonic acids that may be one or more of the group consisting of amino-trismethyl phosphonic acid, hydroxy-ethyl diphosphonic acid and diethylene triamin-pentaphosphonic acid. These phosphonates may be employed with an amount ranging from 0.1 to 8.0%wt, and more preferably from 0.1 to 4.0%wt.

[0020] The composition may further comprise other sequestrants contributing to the objectives outlined above, such as sodium silicate, sodium gluconate, magnesium chloride, magnesium sulfate, and homo and copolymers of acrylic acid having molecular weight of 4000-70000 Daltons. These auxiliary sequestrants gave good results when their total amount is adjusted to a range between 0.1 and 3.0%wt, and more preferably between 0.5 and 3.0 %wt.

[0021] The composition of the invention may further comprise surface active agents in order to provide a combined solution that is able to improve wetting performance of the bath liquor. The preferred surfactants of the invention may be any of the anionic or nonionic surfactants known to those skilled in the art, and in a preferred embodiment, they may be selected from the group consisting of C11-18 alkane sulfonates, C8-C15 alkyl sulfates, C8-C13 fatty alcohols ethoxylated with 3-30 moles of ethylene oxide, and phosphate esters of said alcohols. In a preferred embodiment, total amount of the surfactants within the composition is arranged to be in the range of 0.1 to 10.0 %wt, and more preferably of 0.5 to 5.0% wt. In a most preferred embodiment, the composition of the present invention comprises tridecyl alcohol (C13) ethoxylated with 6 moles of ethylene oxide, an oxo alcohol (C11-12) ethoxylated with 6 moles of ethylene oxide and an alkane sulfonate (C12-14) wherein the total amount of the surfactants range from 1.2 to 8.2% wt.

[0022] While carrying out the objectives of the present invention, the inventors have unexpectedly noted that modifying phosphonate compounds into an N-oxide alkaline salt and using the same as a stabilizer considerably improves the stability profile of the composition. Although the reason is not yet well established, this effect has been attributed to the fact that, while the phosphate groups of these compounds function to eliminate the transition metals such as Fe and Cu

from the media, the amine groups do not react with peroxides because the oxygen atoms deactivate them and prevent loss of peroxide. These modified phosphonates have the following general formula:

$$O^{-}N^{+}(CH_2PO_3M_2)_3$$

wherein,
M is an alkali metal, and preferably potassium or sodium.

[0023] In a preferred embodiment, the compound as identified above is N-oxide potassium salt of amino trimethylene triphosphonic acid.

[0024] With the above composition of the present invention, the inventors noted further advantages over prior art in terms of safety and efficiency upon using the above composition in well-known bleaching processes. In more detail, the composition of the invention found to be less hazardous as compared to the conventional bleaching compositions having high peroxide content which do not involve the phosphonate stabilizers of the invention. These features are assayed and results were noted as explained in the examples.

[0025] According to the second aspect, there is provided a novel process for treating textile articles such as fabric yarns and cellulosic fibers. The process involves use of the composition of the present invention by impregnating the textile article into a process bath involving the composition as identified above or spraying this composition onto said textile article either with a continuous or batch manner. The composition of the present invention is suitable to be used with conventional bleaching processes such as jigger, dip float, continuous bleaching, winch beck, jetting, overflow, pad batch, pad roll and pad steam.

[0026] According to the third aspect of the present invention, novel textile articles treated with the composition of the present invention are provided. These textile materials are noted as being perfectly bleached without substantial loss of gravity and density as opposed to the textile articles treated with conventional peroxide solutions lacking of the phosphonic acid derivatives of the invention. This effect is also illustrated in the following examples.

[0027] The examples as given below are mainly illustrative and showing the technical effects of the present invention. They do not limit the scope of the invention to any particular embodiment.

Example 1. Composition

[0028] $MgCl_2$ was dissolved in 120g of deionized water, and the solution was added of 10g (C12-14, a paraffin mixture) alkane sulfonate, 25g of tridecyl alcohol ethoxylated with 6 moles ethylene oxide, and 30g of oxo alcohol ethoxylated with 6 moles ethylene oxide. After stirring the medium at room temperature until reaching a homogenous solution, 12g of diethylenetriamin penta-methylene phosphonic acid and 17g of N-oxide potassium salt of amino trimethylene triphosphonic acid were added to the medium. The solution as obtained was poured into 782 g aqueous peroxide solution (50%) resulting in the bleaching composition of the invention.

Example 2. Stability

[0029] A bleaching composition was prepared according to example 1 with the exception that N-oxide potassium salt as mentioned above was absent in the composition. This composition and the composition as obtained according to the procedure of example 1 were placed in plastic bottles. Two samples obtained from the first and second composition were treated with a METTLER TOLEDO titration device using $KMnO_4$ and peroxide concentrations were noted.

[0030] The compositions were stored at 25°C for 4-months. At the end of this procedure two samples were treated with the same titration procedure to determine the peroxide concentration. The results showed that the composition of example 2 was able to keep the peroxide at 83% while the composition of example 1 held the peroxide content at 96% as compared to their initial contents in the respective bottles.

Example 3. Safety

[0031] A bleaching composition was prepared according to example 1 with the exception that equivalent amount of $MgCl_2$ was used instead of the phosphonic acid and N-oxide potassium salt as mentioned above.

[0032] A sheep spleen divided into two pieces was immersed into the compositions of Example 1 and Example 3. The first piece in the composition of Example 1 started to rot after about 90 seconds while the second piece in the composition of Example 3 showed rotting within 30 seconds.

Example 4. Textile product treated with the composition

[0033] A bath liquor consisting of 50kg of a bleaching composition prepared according to the proportions of Example

1 and 10kg of NaOH was provided. A similar bath having a composition of example 3 with same amount of NaOH was also provided.

[0034] Two parties of 50 kg woven fabric were treated with these liquors under a continuous impregnation process, and they were dried with hot air steam. Then the weights of the dry fabrics were measured. The weight of the fabric treated with the composition of example 1 lost 1.5 kg of fabric material while the second party treated with the composition of example 3 lost 4.2 kg from its overall weight. The first party was also showing perfectly bleached surface while the second one was showing local faint stains because of the metal ion complexes deposited on the surface.

Claims

1. A bleaching composition comprising;

    a. 25 to 50% wt of hydrogen peroxide,
    b. 0.1 to 8.0% wt of an amino alkyl phosphonate,
    c. 0.1 to 3.0% wt of a metal ion complexing sequestrant, and
    d. complementary amount of deionized water.

2. A bleaching composition according to claim 1 wherein the amount of amino alkyl phosphonate ranges from 0.1 to 4.0%wt.

3. A bleaching composition according to claim 1 wherein the amino alkyl phosphonate is selected from the group consisting of amino-trismethyl phosphonic acid, hydroxy-ethyl diphosphonic acid and diethylene triamin-pentaphosphonic acid.

4. A bleaching composition according to claim 1 wherein the sequestrant has an amount ranging from 0.5 to 3.0%wt, and is selected from the group consisting of sodium silicate, sodium gluconate, magnesium chloride, magnesium sulfate, and homo and copolymers of acrylic acid having molecular weight of 4000-70000 Daltons.

5. A bleaching composition according to claim 1 further comprising a phosphonate derivative having the following general formula:

$$O^{-}N^{+}(CH_2PO_3M_2)_3$$

    wherein M is an alkali metal.

6. A bleaching composition according to claim 5 wherein M is potassium or sodium.

7. A bleaching composition according to claim 5 wherein the phosphonate derivative is N-oxide potassium salt of amino trimethylene triphosphonic acid.

8. A bleaching composition according to claim 1 wherein the composition further comprises a surface active agent in an amount ranging from 0.1 to 10.0%wt.

9. A bleaching composition according to claim 8 wherein the amount of said surface active agent ranges from 0.5 to 5.0%wt, and is selected from the group consisting of C8-C15 alkyl sulfates, C8-C13 fatty alcohols ethoxylated with 3-30 moles of ethylene oxide, and phosphate esters of said alcohols.

10. A bleaching composition according to claim 9 wherein said surface active agent is selected from the group of tridecyl alcohol (C13) ethoxylated with 6 moles of ethylene oxide, oxo alcohol (C11-C12) ethoxylated with 6 moles of ethylene oxide and alkyl sulfates (C8-C15).

11. A method for the preparation of the composition of claim 1 comprising the steps of mixing and preparing a solution of an amino alkyl phosphonate and a metal ion complexing sequestrant, and pouring said solution into hydrogen peroxide, wherein amounts of the ingredients are arranged as in claim 1.

12. A method according to claim 11 wherein the method further comprises addition of a phosphonate derivative having the following general formula:

$$O^{-}N^{+}(CH_2PO_3M_2)_3$$

wherein, M is an alkali metal.

13. A method according to claim 12 wherein the phosphonate derivative is N-oxide potassium salt of amino trimethylene triphosphonic acid.

14. A process for bleaching a textile article comprising treatment of said article with a bleaching composition according to any of the preceding claims.

15. A textile article treated according to the process of claim 14.

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EUROPEAN SEARCH REPORT

Application Number
EP 11 17 6180

DOCUMENTS CONSIDERED TO BE RELEVANT

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	9 January 2012	Menard, Claire

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

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