(19)

(12)





(11) EP 1 837 395 A2

EUROPEAN PATENT APPLICATION

(43) Date of publication: 26.09.2007 Bulletin 2007/39	(51) Int Cl.: <i>C11D 3/395</i> ^(2006.01) <i>C11D 3/20</i> ^(2006.01) <i>C11D 17/04</i> ^(2006.01)
(21) Application number: 07102647.0	
(22) Date of filing: 19.02.2007	
 (84) Designated Contracting States: AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IS IT LI LT LU LV MC NL PL PT RO SE SI SK TR Designated Extension States: AL BA HR MK YU 	 (72) Inventors: Bianchetti, Giulia Ottavia 00144 Rome (IT) Resta, Stefano 00045 Genzano (Roma) (IT) Grande, Giovanni 00136 Roma (IT)
(30) Priority: 17.03.2006 EP 06111339	
(71) Applicant: The Procter and Gamble Company Cincinnati, Ohio 45202 (US)	 (74) Representative: Kellenberger, Jakob NV Procter & Gamble Services Company SA, Temselaan 100 1853 Strombeek-Bever (BE)
(E4) Presses of blooching fobric	

(54) **Process of bleaching fabric**

(57) The present invention encompasses a process of pretreating a fabric which comprises the steps of applying a liquid bleaching composition in its neat form onto said fabric and allowing said composition to remain in contact with said fabric for an effective amount of time before said fabric is washed and/or rinsed, wherein said composition comprises chlorine dioxide. The present invention further encompasses the use of a composition comprising chlorine dioxide in laundry pretreatment.

Printed by Jouve, 75001 PARIS (FR)

Description

Technical field

⁵ **[0001]** The present invention relates to a process of treating fabrics with bleaching compositions. Said compositions are intended for use in laundry applications, and in particular, are intended to be used as laundry pretreater and in a process of pretreating fabrics.

Background of the invention

10

15

[0002] Bleach-containing compositions for bleaching fabrics are well known in the art. They have been extensively described in laundry applications as laundry detergents, laundry additives or laundry pretreaters.

[0003] Indeed, it is known to use such bleach-containing compositions in laundry pretreatment applications to boost the removal of encrusted stains/soils and "problem" stains, such as grease, coffee, tea, grass, mud/clay-containing soils, which are otherwise particularly difficult to remove by typical machine washing.

[0004] However, a drawback associated with such bleach-containing compositions is that they do not always have good bleaching performance.

[0005] Bleaching compositions can be classified into peroxide bleaching compositions and hypochlorite bleaching compositions. Peroxygen bleaches have the advantage over hypochlorite bleaching compositions that are generally

20 considered as being somewhat safer to fabrics, in particular on colored fabric. Although these bleaching compositions provide good bleaching performance when used to treat a soiled fabric, there is still substantial room for further improvement regarding bleaching performance in pretreatment conditions.

[0006] Accordingly, the present invention solves the long-standing need for an effective, bleaching composition with good stains/soils removal performance. Thus, it is an object of the invention to provide a process of pretreating a fabric which provides improved bleaching performances. In detail, it is an object of the present invention to provide excellent

25 which provides improved bleaching performances. In detail, it is an object of the present invention to provide excellent bleach performance in the application wherein said compositions are left neat in contact with said fabrics, before washing said fabrics, i.e. as a laundry pretreater application. **100071** It has now have found that this can be achieved by formulating a chloring disvide bleach containing composition.

[0007] It has now been found that this can be achieved by formulating a chlorine dioxide bleach-containing composition. The present invention is thus based on the finding that the use of chlorine dioxide in a bleaching composition provides

- 30 excellent bleaching performance when said composition is used as a laundry pretreater. Indeed, an advantage associated to the present invention is that the bleaching performance is increased by comparison to classic bleaches. The composition containing chlorine dioxide has especially good result when it is used in pretreatment, for treating set-in stains. By "set-in stains" is to be understood herein stains which are difficult to remove from fabrics even after several washes with classical detergents, or even after bleach pretreatment and washing.
- ³⁵ **[0008]** Moreover, another advantage associated to the present invention is that the colour damage to fabrics is reduced by comparison to hypochlorite. Indeed, the colour change and/or discolouration observed when pretreating soiled coloured fabrics with a composition comprising a chlorine dioxide, according to the present invention, is reduced, as compared to the colour change and/or discolouration observed when using hypochlorite.
- [0009] Chlorine dioxide is a well-known disinfecting and sterilizing agent. However, because it is gaseous at room temperature and atmospheric pressure, chlorine dioxide has not achieved widespread use except where its gaseous nature can be used to effect, for example, in the treatment of water supplies. Despite this problem, chlorine dioxide bleach-containing compositions have been described in the art; the use of chlorine dioxide in low concentrations has long been recognized as useful for the treatment of odours and microbes, notably as a hard surface cleaner.
- [0010] WO 2005/035708 discloses a method for cleaning items comprising a chlorine dioxide composition, wherein
 the chlorine dioxide and the laundry detergent are added to the cleaning apparatus with a water source at the same time.
 [0011] JP 59-157,375 relates to a method for cleaning wet hand towels using stabilized chlorine dioxide mixed with water in the final rinse cycle.

Summary of the invention

50

55

[0012] The present invention encompasses a process of pretreating a fabric which comprises the steps of applying a liquid bleaching composition in its neat form onto said fabric and allowing said composition to remain in contact with said fabric for an effective amount of time before said fabric is washed and/or rinsed, wherein said composition comprises chlorine dioxide. The present invention further encompasses the use of a composition comprising chlorine dioxide in laundry pretreatment.

Detailed description of the invention

[0013] In a first aspect, the present invention encompasses a process of pretreating a fabric, which comprises the steps of contacting said fabric with a bleaching composition in its neat form wherein said bleaching composition comprises chlorine dioxide. Preferably, the composition containing chlorine dioxide is a liquid aqueous bleaching composition.

- **[0014]** In a preferred embodiment, the composition according to the invention comprises from 0.0001 % to 10% by weight of the total composition of chlorine dioxide, preferably from 0.001 % to 2% by weight and more preferably from 0.01 % to 0.5%.
- [0015] The present invention encompasses a process of pretreating a fabric, which comprises the steps of applying
 a liquid bleaching composition containing chlorine dioxide, in its neat form onto a fabric and allowing said composition
 to remain in contact with said fabric for an effective amount of time, before said fabric is washed and/or rinsed.
 [0016] The composition remains in contact with said fabric for an effective amount of time, two contact with said fabric for a period of 1.
 - **[0016]** The composition remains in contact with said fabric for an effective amount of time, typically for a period of 1 minute to 24 hours, preferably 1 minute to 1 hour and more preferably 5 minutes to 30 minutes. More preferably, the composition remains in contact with the fabric without leaving said composition to dry onto said fabric.
- ¹⁵ **[0017]** Optionally, when the fabric is soiled with encrusted stains/soils which otherwise would be relatively difficult to remove, the compositions may be rubbed and/or brushed more or less intensively, for example, by means of a sponge or a brush or simply by rubbing two pieces of fabric each against the other.

[0018] The compositions comprising chlorine dioxide are used in a process of pretreating fabric. By "to pretreat fabrics" it is to be understood that the liquid composition is applied in its neat form onto the soiled fabric and left to act onto said

- 20 fabric before said fabric is washed and/or rinsed. By "in its neat form" it is to be understood that the compositions described herein are applied onto the fabrics to be treated without undergoing any dilution prior the application by the user. [0019] By "washing", it is to be understood herein that the fabrics are contacted with a conventional detergent composition, preferably comprising at least one surface active agent in an aqueous bath, this washing may occur by means of a washing machine or simply by hands. In a preferred embodiment, the washing step according to the present invention
- ²⁵ is performed in a washing machine. The conventional laundry detergent may be delivered into the washing machine either by charging the dispenser drawer of the washing machine with the detergent or by directly charging the drum of the washing machine with the detergent. By "conventional laundry detergent" it is meant herein, a laundry detergent composition currently available on the market. Preferably, said conventional laundry detergent comprises at least one surface active agent ("surfactant" as described herein below). Said laundry detergent compositions may be formulated
- ³⁰ as powders, liquids or tablets. Suitable laundry detergent compositions are for example DASH futur®, DASH essential®, DASH liquid®, ARIEL tablets® and other products sold under the trade names ARIEL® or TIDE®. By "fabrics", it is meant herein any type of fabrics including clothes, curtains, drapes, bed linens, bath linens, table cloths, sleeping bags, tents and the like. Fabrics to be treated as described herein include natural fabrics (e.g., fabrics made of cotton, viscose, and linen), synthetic fabrics such as those made of polymeric fibers of synthetic origin as well as
- those made of both natural and synthetic fibers.
 [0020] Furthermore, the compositions according to the invention may be used in so-called commercial laundry applications. Indeed, the compositions herein may be used as pretreaters in a large scale commercial bleaching process
 [0021] Upon application onto fabrics, the chlorine dioxide present in the liquid bleaching composition may results from chlorine dioxide, which is already present in the composition, or may be produced immediately prior to the application,
- ⁴⁰ i.e. in the dispersing step, for example by mixing in a premix chamber of the container wherein said composition is packaged in, or in the stream of liquid dispensed from the container

wherein said composition is packaged, or may be produced directly on the fabrics, i.e. "in-situ".

[0022] A stabilized raw material containing chlorine dioxide (such as for example the Carnebon 200® from International Dioxcide Inc) can be use to formulate a composition containing chlorine dioxide. This raw material is added to a liquid aqueous composition, in the purpose of obtaining a composition containing stabilized chlorine dioxide.

[0023] There are several ways of obtaining chlorine dioxide in-situ or immediately prior to the application onto fabrics according to the process of the invention.

[0024] The chlorine dioxide can be generated by acidification of a chlorine dioxide precursor, such as sodium chlorite $(NaClO_2)$ or sodium chlorate $(NaClO_3)$, with an acid source:

50

45

5

$$5 \text{ CIO}_2^- + 4\text{H}^+ \rightarrow 4 \text{ CIO}_2 + 2 \text{ H}_2\text{O} + \text{CIO}_2$$

$$\mathsf{NaClO}_3 \texttt{+} \texttt{1/2} \texttt{H}_2\mathsf{O}_2 \texttt{+} \texttt{H}_2\mathsf{SO}_4 \rightarrow \mathsf{ClO}_2 \texttt{+} \texttt{NaHSO}_4 \texttt{+} \texttt{H}_2\mathsf{O} \texttt{+} \texttt{1/2} \texttt{O}_2$$

⁵⁵ **[0025]** Chlorine dioxide can also be obtained by other means such as, for example, the oxidation of sodium chlorite by persulfate:

$$2 \text{ NaClO}_2 + \text{Na}_2\text{S}_2\text{O}_8 \rightarrow 2 \text{ ClO}_2 + 2 \text{ Na}_2\text{SO}_4;$$

[0026] Chlorine dioxide can also be obtained by the reduction of chloric acids (HClO₃) with oxalic acid:

$$2 \text{ HClO}_3 + \text{H}_2\text{C}_2\text{O}_4 \rightarrow 2 \text{ ClO}_2 + 2 \text{ CO}_2 + 2 \text{ H}_2\text{O};$$

5

10

15

[0027] According to the present invention, the preferred way of obtaining chlorine dioxide is to generate chlorine dioxide by acidification of a chlorine dioxide precursor, such as sodium chlorite $(NaClO_2)$ or sodium chlorate $(NaClO_3)$, with an acid source, such as for example citric acid $(HOC(COOH)(CH_2COOH)_2)$ or oxalic acid $(H_2C_2O_4)$. In a more preferred way, the chlorine dioxide is generated by acidification of sodium chlorite $(NaClO_2)$ with an acid source, such as for example citric acid the control of sodium chlorite $(NaClO_2)$ with an acid source, such as for example citric acid the control of sodium chlorite $(NaClO_2)$ with an acid source, such as for example citric acid.

[0028] The compositions herein can be packaged in a variety of containers including conventional bottles, bottles equipped with roll-on, sponge, brusher or sprayers, wipes or multi-compartments container package.

[0029] In a preferred embodiment, the composition herein is applied onto said fabric by combining two components, these components are packed in such way as to be kept physically separated from each other prior to their use, as for example a combination of a wipe and a liquid activator composition. In a preferred embodiment, said composition is applied onto said fabric by means of a wipe, the wipe is a pre-moistened or a pre-loaded wipes. A liquid activator is

applied to the wipe in order to produce the chlorine dioxide at the time of the addition.[0030] In a more preferred embodiment, in a multi-compartment, preferably a two compartments package. In all such embodiments the key measure is that the reactants are combined only at the time of cleaning.

20 **[0031]** In a preferred embodiment according to the invention, the package is a multi-compartment container, preferably a two compartments container. The package is designed to keep the composition in two components, i.e., in a first and in a second component.

[0032] There are several ways of mixing the first and the second components. This mixing can be done within a mixing zone adjacent to the outlets of the first and second compartments or into a mixing chamber forming part of the container.

- However with this kind of arrangement steps may need to be taken to avoid contamination of the contents of the chambers. The container can also be designed to issue separate first and second components of compositions which are mixed substantially only when contacting the fabrics or even, the container can be designed to allow the first and second components to be mixed during the stream of the products to the fabrics. In a preferred embodiment, according to the process of the invention, the container is designed to mix the separate first and second components of compositions only when contacting the fabrics, thus the chlorine dioxide is generated in-situ.
- [0033] This multi-compartment container can be a spray execution, or a bottle with two nozzles at the end.
 [0034] In a preferred embodiment, wherein said multi-compartment container does not have a mixing outlet, the mixing
- step can be performed in a dosing cup wherein the two components are premixed before the application on the stain. This container has the purpose to facilitate the deposition/mixing/scrubbing of the two different components on the stain.
- ³⁵ **[0035]** Containers suitable for use in this aspect of the invention are well known. According to the invention, the multicompartments container has the form of a multi-compartments bottle or spray. Examples include two-compartments trigger sprays having a mechanical pumping action and side-by-side twin squeeze bottle chambers having simple narrowed nozzle outlets. In an even more preferred embodiment, the multi-compartment container herein is a multi-compartment bottle or spray.
- 40 [0036] The first and second components of compositions can also be separated in two different phases in the same composition; the mixing of the two components is achieved by shaking such a composition.
 [0037] In a preferred way of obtaining the composition, according to the invention, comprising chlorine dioxide, is provided by a system which comprises two components wherein the first component comprises a chlorine dioxide precursor and the second component comprises a chlorine dioxide activator, which, on admixture with the first component,
- ⁴⁵ reacts with the precursor to form chlorine dioxide. [0038] The chlorine dioxide precursors are compounds which result in the formation of the chlorite ion (CIO²⁻) or of the chlorate ion (CIO³⁻). The chlorine dioxide precursors can be chosen from the group consisting of sodium chlorite (NaCIO₂), sodium chlorate (NaCIO₃), potassium chlorite (KCIO₂), potassium chlorate (KCIO₃), lithium chlorite (LiCIO₂), lithium chlorate (LiCIO₃), chlorous acid (HCIO₂) or chloric acid (HCIO₃).
- [0039] Preferably, the chlorine dioxide precursor is sodium chlorite or sodium chlorate. More preferably the chlorine dioxide precursor is the sodium chlorite.
 [0040] In a preferred embodiment, the chlorine dioxide activator is an acid source, such as for example citric acid or oxalic acid. In a more preferred embodiment the chlorine dioxide activator is citric acid.
- [0041] In a preferred embodiment, the chlorine dioxide is generated by mixing sodium chlorite (NaClO₂) with a source of acidity or an acid. Therefore, in a preferred embodiment, the chlorine dioxide precursor is sodium chlorite and the activator is a source of acidity.

[0042] In another preferred embodiment, the chlorine dioxide is generated by the oxidation of sodium chlorite (NaClO₂) with sodium persulfate (Na₂S₂O₈). Therefore, in a preferred embodiment, the chlorine dioxide precursor is sodium chlorite.

[0043] In another preferred embodiment, the chlorine dioxide is generated by a mix of sodium chlorate (NaClO₃) with hydrogen peroxide (H_2O_2) and with an acidic source such as sulphuric acid (H_2SO_4) for example.

[0044] Therefore, in another preferred embodiment, the chlorine dioxide is generated by a mix of chloric acids (HClO₃) with oxalic acid ($H_2C_2O_4$).

- 5 [0045] Thus, more particularly, the present invention further encompasses a process of treating a fabric by applying onto said fabric a composition comprising chlorine dioxide, wherein said composition is packaged in a multi-compartment container having at least two compartments, wherein a first compartment comprises a composition containing a chlorine dioxide precursor and wherein a second compartment comprises a composition containing a chlorine dioxide activator. [0046] In the preferred embodiment, the compositions in the first compartment comprise a chlorine dioxide precursor.
- ¹⁰ The chlorine dioxide precursor, in the first compartment, may be present, in the composition, from 0.005% to 20% by weight of the total composition, preferably from 0.01% to 5% by weight and more preferably from 1% to 3%. [0047] The two compositions are mixed upon use to form the bleaching composition herein. Upon mixing of the composition, the chlorine dioxide precursor, such as, for example sodium chlorite (NaClO₂) or sodium chlorate (NaClO₃), is in an acidic composition, and releases the chlorine dioxide. The acidic composition is present in an excess amount
- in order to acidify the first composition.
 [0048] Preferably, the composition comprising a chlorine dioxide precursor is formulated in the neutral or in the alkaline pH range. It is within this neutral to alkaline pH range that the composition has its optimum chemical stability and performance. Accordingly, the composition has preferably a pH equal or above 7. The composition in the second compartment, comprising a chlorine dioxide activator, is preferably formulated to be acidic, i.e. has a pH below 7. More preferably, the composition is formulated to have a pH comprise between 1 and 5. In a more preferred embodiment, the

[0049] In a preferred embodiment, the composition comprising a chlorine dioxide precursor is an alkaline or neutral composition and the composition comprising a chlorine dioxide activator is an acidic composition. Wherein upon mixing of the alkaline composition and the acidic composition the resulting admixing composition is acidic and generates chlorine

25 dioxide.

[0050] Accordingly, the compositions herein may further comprise an acid or a base to adjust the pH as appropriate. Preferred acids herein are organic or inorganic acids or mixtures thereof. Preferred organic acids are acetic acid, succinic acid, citric acid or a mixture thereof. Preferred inorganic acids are sulphuric acid, phosphoric acid or a mixture thereof. A particularly preferred acid to be used herein is an organic acid and most preferred is citric acid.

³⁰ **[0051]** Another particularly preferred acid to be used herein is succinic acid. Indeed, the succinic acid when used in the process according to the present invention has the advantage to provide color safety by comparison with other organic acid.

[0052] Typical levels of such acids, when present, are of from 0.01% to 10%, preferably from 0.1% to 5% and more preferably from 1% to 3% by weight of the total composition. The bases to be used herein can be organic or inorganic

- ³⁵ bases. Suitable bases for use herein are the caustic alkalis, such as sodium hydroxide, sodium carbonate, potassium hydroxide and/or lithium hydroxide, and/or the alkali metal oxides such as sodium and/or potassium oxide or mixtures thereof. Other suitable bases include ammonia, ammonium carbonate and hydrogen carbonate. A preferred base is sodium carbonate. Typical levels of such bases are of from 0.001% to 1.0%, preferably from 0.05% to 5% and more preferably from 0.01% to 1% by weight of the total composition.
- ⁴⁰ **[0053]** In a preferred embodiment, the present invention encompasses a process of treating a fabric with a composition comprising chlorine dioxide and a peroxygen bleach. This composition, containing chlorine dioxide and peroxygen bleach, provides excellent stain removal performance and, in the same time, provides color safety.

[0054] Preferably, the composition comprises peroxygen bleach. More preferably, when the composition is packed in a two compartments container, the peroxygen bleach is present in the composition containing the chlorine dioxide activator.

[0055] Preferred peroxygen bleach is hydrogen peroxide, or a water soluble source thereof, or mixtures thereof. As used herein a hydrogen peroxide source refers to any compound which produces hydrogen peroxide when said compound is in contact with water. Preferably the composition contains hydrogen peroxide or a water soluble source thereof, more preferably the composition, according to the invention, contains hydrogen peroxide.

- 50 [0056] Suitable water-soluble sources of hydrogen peroxide for use herein include percarbonates, persilicates, persulphates such as monopersulfate, perborates, peroxyacids such as diperoxydodecandioic acid (DPDA), magnesium perphtalic acid, perlauric acid, perbenzoic and alkylperbenzoic acids, hydroperoxides, aliphatic and aromatic diacyl peroxides, and mixtures thereof. Preferred peroxygen bleaches herein are hydrogen peroxide, hydroperoxide and/or diacyl peroxide. Suitable hydroperoxides for use herein are tert-butyl hydroperoxide, cumyl hydroperoxide, 2,4,4-trimeth-
- 55 ylpentyl-2-hydroperoxide, di-isopropylbenzene-monohydroperoxide, tert-amyl hydroperoxide and 2,5-dimethyl-hexane-2,5-dihydroperoxide. Suitable aliphatic diacyl peroxides for use herein are dilauroyl peroxide, didecanoyl peroxide, dimyristoyl peroxide, or mixtures thereof. Suitable aromatic diacyl peroxide for use herein is for example benzoyl peroxide. [0057] In a more preferred embodiment, the compositions suitable to be used herein comprise from 0.01% to 20% by

weight of the total composition of peroxygen bleach preferably from 0.01 % to 10% and most preferably from 1% to 7%. **[0058]** In a preferred embodiment, the present invention encompasses a process of treating a fabric with a composition comprising chlorine dioxide and a dye maintenance agent. Indeed, this composition, containing chlorine dioxide and dye maintenance agents provides excellent stain removal performance and, in the same time, provides color safety.

⁵ [0059] In a more preferred embodiment, the dye maintenance agent will be in the compartment which contains the chlorine dioxide activator. It has now been found that dye maintenance agents in bleaching compositions provide an active color protection benefit. By "active color protection" it is meant herein the active protection of dyed fabrics against discoloration caused by interaction of a wash solution and the fabric dyes ("color protection benefit"). Indeed, color protection in a bleaching composition may be provided independently of a color safety benefit or even in combination of a color safety benefit coming from color safety ingredients.

[0060] Indeed, it has been observed that dye maintenance agents specifically adhere to dye molecules deposited on fabrics, preferably sulphate groups of dye molecules, and thereby reduce the solubility of said dye molecules. Thereby, protecting said dyes from solubilising them off the fabric and thereby discoloring said fabric caused by the interaction of the bleaching composition and/or the wash solution formed by a conventional laundry detergent used in addition to the

- ¹⁵ bleaching composition and the dye. [0061] Any dye maintenance agent known to those skilled in the art are suitable for use herein. Suitable dye maintenance agent are described as cyclic amine based polymers, oligomers or copolymers in WO 99/14301 and dye maintenance polymers or oligomers in WO 00/56849, both documents being incorporated herein by reference.
- [0062] Typically, the bleaching compositions according to the present invention may comprise from 0.001% to 30%, preferably from 0.01 % to 15% and more preferably from 0.05% to 5% by weight of the total composition of a dye maintenance agent.

[0063] In a preferred embodiment the dye maintenance agent is a cyclic amine based polymer, oligomer or copolymer.

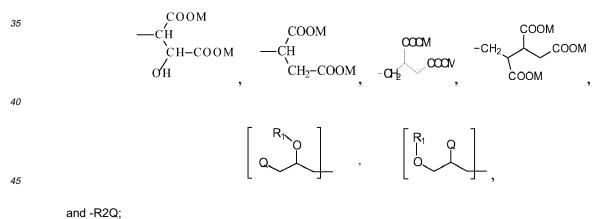
[0064] Preferably, said cyclic amine based polymers, oligomers or copolymers are of the general formula :

25

$$T - \begin{bmatrix} W - R_2 \end{bmatrix}_{x}^{W-T} A_b$$

wherein each T is independently selected from the group consisting of : H, C1-C12 alkyl, substituted alkyl, C7-C12 alkylaryl,

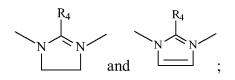
-(CH₂)_hCOOM, -(CH₂)_hSO₃M, CH₂CH(OH)SO₃M, -(CH₂)_hOSO₃M,



wherein W comprises at least one cyclic constituent selected from the group consisting of:

50

 $- \begin{bmatrix} (R_3)_c \\ | \\ N \\ R_3 \end{bmatrix}_q \xrightarrow{(R_3)_c} D \xrightarrow{(R_3)_c} V \xrightarrow{(R_3)_c} \begin{bmatrix} (R_3)_c \\ | \\ N \\ N \\ (D)_c \end{bmatrix}_q \xrightarrow{(R_3)_c} D \xrightarrow{(R_3)_c} \begin{bmatrix} (R_3)_c \\ | \\ R_3 \end{bmatrix}_q \xrightarrow{(R_3)_c} D \xrightarrow{(R_3)_c} \begin{bmatrix} (R_3)_c \\ | \\ R_3 \end{bmatrix}_q \xrightarrow{(R_3)_c} D \xrightarrow{(R_3)_c} \begin{bmatrix} (R_3)_c \\ | \\ R_3 \end{bmatrix}_q \xrightarrow{(R_3)_c} D \xrightarrow{(R_3)_c} \begin{bmatrix} (R_3)_c \\ | \\ R_3 \end{bmatrix}_q \xrightarrow{(R_3)_c} D \xrightarrow{(R_3)_c} \begin{bmatrix} (R_3)_c \\ | \\ R_3 \end{bmatrix}_q \xrightarrow{(R_3)_c} D \xrightarrow{(R_3)_c} D$



5

in addition to the at least one cyclic constituent, W may also comprise an aliphatic or substituted aliphatic moiety of the general structure;

 $- \begin{bmatrix} \begin{pmatrix} R_3 \end{pmatrix}_c \\ 1 \\ N \\ N \\ \vdots \end{bmatrix} = \begin{bmatrix} \begin{pmatrix} R_3 \end{pmatrix}_c \\ 1 \\ N \\ R_3 \end{bmatrix}$

10

15

20

- each B is independently C1-C12 alkylene, C1-C12 substituted alkylene, C3-C12 alkenylene, C8-C12 dialkylarylene, C8-C12 dialkylarylenediyl, and -(R₅O)nR₅-;
- each D is independently C2-C6 alkylene;

each Q is independently selected from the group consisting of hydroxy, C1-C18 alkoxy, C2-C18 hydroxy alkoxy, amino, C1-C18 alkyl amino, dialkyl amino, trialkyl amino groups, heterocyclic monoamino groups and diamine groups;

- each R1 is independently selected from the group consisting of H, C1-C8 alkyl and C1-C8 hydroxyalkyl;

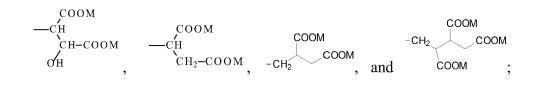
each R2 is independently selected from the group consisting of C1-C12 alkylene, C1-C12 alkenylene, -CH₂-CH
 (OR₁)-CH₂, C8-C12 alkarylene, C4-C12 dihydroxy alkylene, poly(C2-C4 alkyleneoxy)alkylene, H₂CH(OH)
 CH₂OR2OCH₂CH(OH)CH₂-, and C3-C12 hydrocarbyl moieties; provided that when R2 is a C3-C12 hydrocarbyl moiety the hydrocarbyl moiety can comprise from 2 to 4 branching moieties of the general structure:

30

$$(-OR_5)_{r}O-CH_2-CH-CH_2 + W-R_2 + W-T$$

each R3 is independently selected from the group consisting of H, R2, O, C1-C20 hydroxyalkyl, C1-C20 alkyl, substituted alkyl, C6-C11 aryl, substituted aryl, C7-C11 alkylaryl, C1-C20 aminoalkyl, -(CH₂)_hCOOM, -(CH₂)_hSO₃M, CH₂CH(OH)SO₃M, -(CH₂)_hOSO₃M,

40



45

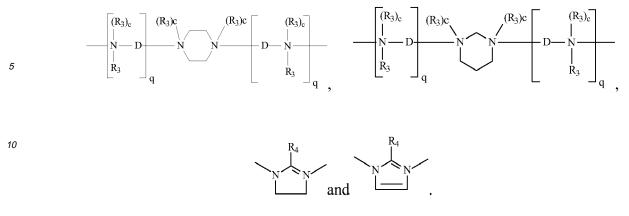
wherein at least about 10 mole%, preferably at least about 20 mole%, more preferably at least about 30 mole%, and most preferably at least about 50 mole% of the R3 groups are O, provided that O is only present on a tertiary N;

- each R4 is independently selected from the group consisting of H, C1-C22 alkyl, C1-C22 hydroxyalkyl, aryl and C7-C22 alkylaryl;

- 50 C22 alkylaryl;
 - each R5 is independently selected from the group consisting of C2-C8 alkylene, C2-C8 alkyl substituted alkylene; and A is a compatible monovalent or di or polyvalent anion; M is a compatible cation; and wherein b = number necessary to balance the charge; each x is independently from 3 to 1000; each c is independently 0 or 1; each h is independently from 1 to 8; each q is independently from 0 to 6; each n is independently from 1 to 20; each r is independently from 0 to 20; and each t is independently from 0 to 1.

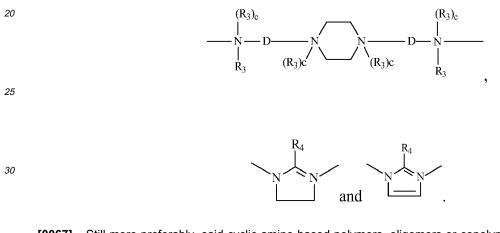
55

[0065] More preferably, said cyclic amine based polymers, oligomers or copolymers are of the above formula, wherein each R1 is H and at least one W is selected from the group consisting of:



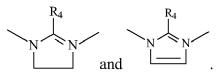
15

[0066] Even more preferably, said cyclic amine based polymers, oligomers or copolymers are of the above formula, wherein R1 is H and at least one W is selected from the group consisting of:



[0067] Still more preferably, said cyclic amine based polymers, oligomers or copolymers are of the above formula, wherein each R1 is H and at least one W is selected from the group consisting of:

40



[0068] In a preferred embodiment according to the present invention, said cyclic amine based polymers, oligomers or copolymers are oxidized adducts selected from the group consisting of piperazine, piperidine, epichlorohydrin, epichlorohydrin benzyl quat, epichlorohydrin methyl quat, morpholine and mixtures thereof.

[0069] In another preferred embodiment according to the present invention, the dye maintenance agent herein is imidazole : epi-chlorohydrin copolymer (condensation oligomer of imidazole and epi-chlorohydrin at a ratio of 1:4:1).

- [0070] In another preferred embodiment, the present invention encompasses a process of treating a fabric with a composition comprising chlorine dioxide and Chlorine scavengers. Indeed, this composition, containing chlorine dioxide and Chlorine scavengers provides excellent stain removal performance and, in the same time, provides color safety.
 [0071] Chlorine scavengers are actives that react with chlorine, or with chlorine-generating materials, to eliminate or reduce the bleaching activity of the chlorine materials.
- [0072] A chlorine scavengers is preferably selected from the group consisting of: amines and their salts; ammonium salts; amino acids and their salts; polyamino acids and their salts; polyethyleneimines and their salts; polyamines and their salts; polyamines; polyamines;

[0073] Non-limiting examples of chlorine scavengers include amines, preferably primary and secondary amines, including primary and secondary fatty amines, and alkanolamines; and their salts; ammonium salts, e.g., chloride, bromide,

citrate, sulfate; amine-functional polymers and their salts; amino acid homopolymers with amino groups and their salts, such as polyarginine, polylysine, polyhistidine; amino acid copolymers with amino groups and their salts, including 1,5di-ammonium-2-methyl-panthene dichloride and lysine monohydrochloride; amino acids and their salts, preferably those having more than one amino group per molecule, such as arginine, histidine, and lysine, reducing anions such as sulfite,

- ⁵ bisulfite, thiosulfate, nitrite, and antioxidants such as ascorbate, carbamate, phenols; and mixtures thereof. Preferred chlorine scavengers are water soluble, especially, low molecular weight primary and secondary amines of low volatility, e.g., monoethanolamine, diethanolamine, tris(hydroxymethyl)aminomethane, hexamethylenetetramine, and their salts, and mixtures thereof. Suitable chlorine scavenger polymers include: water soluble amine-functional polymers, e.g., polyethyleneimines, polyamineamides, polyacrylamides, and their salts, and mixtures thereof. The chlorine
- scavengers is more preferably selected from the group consisting of monoethanolamine, diethanolamine, triethanolamine, and mixtures thereof. A more preferred polyamine is the Monoethanolamine.
 [0074] Liquid bleaching compositions of the present invention are aqueous and therefore, preferably they may comprise water, more preferably may comprise water in an amount of from 60% to 98%, even more preferably of from 80% to 97% and most preferably 85% to 97% by weight of the total composition.
- ¹⁵ **[0075]** The compositions herein, may further comprise a variety of other optional ingredients such as chelating agents, builders, surfactants, stabilisers, bleach activators, soil suspenders, soil suspending polyamine polymers, polymeric soil release agents, foam reducing systems, radical scavengers, catalysts, dye transfer agents, brighteners, perfumes, hydrotropes, pigments and dyes.
- 20 Surfactants:

[0076] The compositions may further comprise a surfactant including nonionic surfactants, zwiterrionic surfactants, anionic surfactants, cationic surfactants and/or amphoteric surfactants. Highly preferred compositions comprise a non-ionic surfactant or a zwiterrionic betaine surfactant or a mixture thereof.

²⁵ **[0077]** Typically, the compositions may comprise from 0.01% to 30%, preferably from 0.1% to 25% and more preferably from 0.5% to 20% by weight of the total composition of a surfactant.

[0078] Suitable nonionic surfactants include alkoxylated nonionic surfactants. Preferred alkoxylated nonionic surfactants herein are ethoxylated nonionic surfactants according to the formula $\text{RO}-(\text{C}_2\text{H}_4\text{O})_n\text{H}$, wherein R is a C_6 to C_{22} alkyl chain or a C_6 to C_{28} alkyl benzene chain, and wherein n is from 0 to 20, preferably from 1 to 15 and, more preferably

- from 2 to 15 and most preferably from 2 to 12. The preferred R chains for use herein are the C₈ to C₂₂ alkyl chains. Propoxylated nonionic surfactants and ethoxy/propoxylated ones may also be used herein instead of the ethoxylated nonionic surfactants as defined herein above or together with said surfactants. Preferred ethoxylated nonionic surfactants are according to the formula above and have an HLB (hydrophilic-lipophilic balance) below 16, preferably below 15, and more preferably below 14. Those ethoxylated nonionic surfactants have been found to provide good grease cutting properties.
- **[0079]** Accordingly suitable ethoxylated nonionic surfactants for use herein are Dobanol® 91-2.5 (HLB= 8.1; R is a mixture of C9 and C₁₁ alkyl chains, n is 2.5), or Lutensol® TO3 (HLB=8; R is a C₁₃ alkyl chains, n is 3), or Lutensol® A03 (HLB=8; R is a mixture of C₁₃ and C₁₅ alkyl chains, n is 3), or Tergitol® 25L3 (HLB= 7.7; R is in the range of C₁₂ to C₁₅ alkyl chain length, n is 3), or Dobanol® 23-3 (HLB=8.1; R is a mixture of C₁₂ and C₁₃ alkyl chains, n is 3), or
- ⁴⁰ Dobanol® 23-2 (HLB=6.2; R is a mixture of C₁₂ and C₁₃ alkyl chains, n is 2), or Dobanol® 45-7 (HLB=11.6; R is a mixture of C₁₄ and C₁₅ alkyl chains, n is 7) Dobanol® 23-6.5 (HLB=11.9; R is a mixture of C₁₂ and C₁₃ alkyl chains, n is 6.5), or Dobanol® 25-7 (HLB=12; R is a mixture of C₁₂ and C₁₅ alkyl chains, n is 7), or Dobanol® 91-5 (HLB=11.6; R is a mixture of C₉ and C₁₁ alkyl chains, n is 5), or Dobanol® 91-6 (HLB=12.5; R is a mixture of C₉ and C₁₁ alkyl chains, n is 6), or Dobanol® 91-8 (HLB=13.7; R is a mixture of C₉ and C₁₁ alkyl chains, n is 8), Dobanol® 91-10 (HLB=14.2; R
- ⁴⁵ is a mixture of C₉ to C₁₁ alkyl chains, n is 10), Dobanol® 91-12 (HLB=14.5; R is a mixture of C₉ to C₁₁ alkyl chains, n is 12), or mixtures thereof. Preferred herein are Dobanol® 91-2.5, or Lutensol® TO3, or Lutensol® A03, or Tergitol® 25L3, or Dobanol® 23-3, or Dobanol® 23-2, or Dobanol® 45-7, Dobanol® 91-8, or Dobanol® 91-10, or Dobanol® 91-12, or mixtures thereof. These Dobanol® surfactants are commercially available from SHELL. These Lutensol® surfactants are commercially available from UNION CARBIDE.
- ⁵⁰ **[0080]** Suitable chemical processes for preparing the alkoxylated nonionic surfactants for use herein include condensation of corresponding alcohols with alkylene oxide, in the desired proportions. Such processes are well known to the man skilled in the art and have been extensively described in the art.

[0081] The compositions herein may desirably comprise one of those ethoxylated nonionic surfactants or a mixture of those ethoxylated nonionic surfactants having different HLBs (hydrophilic-lipophilic balance). In a preferred embodi-⁵⁵ ment the compositions herein comprise an ethoxylated nonionic surfactant according to the above formula and having an HLB up to 10 (i.e., a so called hydrophobic ethoxylated nonionic surfactant), preferably below 10, more preferably below 9, and an ethoxylated nonionic surfactant according to the above formula and having a so called hydrophilic ethoxylated nonionic surfactant), preferably from 11 to 14. Indeed, in this preferred embodiment

the compositions typically comprise from 0.01% to 15% by weight of the total composition of said hydrophobic ethoxylated nonionic surfactant, preferably from 0.5% to 10% and from 0.01% to 15% by weight of said hydrophilic ethoxylated nonionic surfactant, preferably from 0.5% to 10%. Such mixtures of ethoxylated nonionic surfactants with different HLBs may be desired as they allow optimum grease cleaning removal performance on a broader range of greasy soils having different hydrophobic/hydrophilic characters.

[0082] Other suitable nonionic surfactants to be used herein include polyhydroxy fatty acid amide surfactants, or mixtures thereof, according to the formula:

R²-C(O)-N(R¹)-Z,

10

5

wherein R¹ is H, or C₁-C₄ alkyl, C₁-C₄ hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl or a mixture thereof, R² is C₅₋C₃₁ hydrocarbyl, and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative thereof.

- **[0083]** Preferably, R¹ is $C_{1-}C_4$ alkyl, more preferably C_1 or C_2 alkyl and most preferably methyl, R² is a straight chain $C_{7-}C_{19}$ alkyl or alkenyl, preferably a straight chain $C_{9-}C_{18}$ alkyl or alkenyl, more preferably a straight chain $C_{11-}C_{18}$ alkyl or alkenyl, or mixtures thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z is a glycityl. Suitable reducing sugars include glucose, fructose, maltose, lactose, galactose, mannose and xylose. As raw materials, high dextrose corn syrup, high fructose corn syrup, and high maltose corn syrup can be utilized as well as the individual sugars listed above. These
- 20 corn syrups may yield a mix of sugar components for Z. It should be understood that it is by no means intended to exclude other suitable raw materials. Z preferably will be selected from the group consisting of -CH₂-(CHOH)_n-CH₂OH,-CH(CH₂OH)-(CHOH)_{n-1}-CH₂OH, -CH₂-(CHOH)₂-(CHOH)₂-(CHOH)-CH₂OH, where n is an integer from 3 to 5, inclusive, and R' is H or a cyclic or aliphatic monosaccharide, and alkoxylated derivatives thereof. Most preferred are glycityls wherein n is 4, particularly CH₂-(CHOH)₄-CH₂OH.
- 25 [0084] In formula R²- C(O) N(R¹) Z, R¹ can be, for example, N-methyl, N-ethyl, N-propyl, N-isopropyl, N-butyl, N-2-hydroxy ethyl, or N-2-hydroxy propyl. R²- C(O) - N< can be, for example, cocamide, stearamide, oleamide, lauramide, myristamide, capricamide, palmitamide, tallowamide and the like. Z can be 1-deoxyglucityl, 2-deoxyfructityl, 1-deoxymaltityl, 1-deoxylactityl, 1-deoxygalactityl, 1-deoxymannityl, 1-deoxymaltotriotityl and the like.
- [0085] Suitable polyhydroxy fatty acid amide surfactants to be used herein may be commercially available under the ³⁰ trade name HOE® from Hoechst.

[0086] Methods for making polyhydroxy fatty acid amide surfactants are known in the art. In general, they can be made by reacting an alkyl amine with a reducing sugar in a reductive amination reaction to form a corresponding N-alkyl polyhydroxyamine, and then reacting the N-alkyl polyhydroxyamine with a fatty aliphatic ester or triglyceride in a condensation/amidation step to form the N-alkyl, N-polyhydroxy fatty acid amide product. Processes for making compositions

- ³⁵ containing polyhydroxy fatty acid amides are disclosed for example in GB patent specification 809,060, published February 18, 1959, by Thomas Hedley & Co., Ltd., US patent 2,965,576, issued December 20, 1960 to E.R. Wilson, US patent 2,703,798, Anthony M. Schwartz, issued March 8, 1955, US patent 1,985,424, issued December 25, 1934 to Piggott and WO92/06070, each of which is incorporated herein by reference.
- [0087] Suitable zwiterrionic betaine surfactants for use herein contain both a cationic hydrophilic group, i.e., a quaternary ammonium group, and anionic hydrophilic group on the same molecule at a relatively wide range of pH's. The typical anionic hydrophilic groups are carboxylates and sulphonates, although other groups like sulfates, phosphonates, and the like can be used. A generic formula for the zwitterionic betaine surfactant to be used herein is:

$R_1-N^+(R_2)(R_3)R_4X^-$

45

- wherein R_1 is a hydrophobic group; R_2 is hydrogen, C_1 - C_6 alkyl, hydroxy alkyl or other substituted C_1 - C_6 alkyl group; R_3 is C_1 - C_6 alkyl, hydroxy alkyl or other substituted C_1 - C_6 alkyl group which can also be joined to R_2 to form ring structures with the N, or a C_1 - C_6 sulphonate group; R_4 is a moiety joining the cationic nitrogen atom to the hydrophilic group and is typically an alkylene, hydroxy alkylene, or polyalkoxy group containing from 1 to 10 carbon atoms; and X is the hydrophilic group, which is a carboxylate or sulphonate group.
- **[0088]** Preferred hydrophobic groups R_1 are aliphatic or aromatic, saturated or unsaturated, substituted or unsubstituted hydrocarbon chains that can contain linking groups such as amido groups, ester groups. More preferred R_1 is an alkyl group containing from 1 to 24 carbon atoms, preferably from 8 to 18, and more preferably from 10 to 16. These simple alkyl groups are preferred for cost and stability reasons. However, the hydrophobic group R_1 can also be an
- ⁵⁵ amido radical of the formula R_a -C(O)-NH-(C(R_b)₂)_m, wherein R_a is an aliphatic or aromatic, saturated or unsaturated, substituted or unsubstituted hydrocarbon chain, preferably an alkyl group containing from 8 up to 20 carbon atoms, preferably up to 18, more preferably up to 16, R_b is selected from the group consisting of hydrogen and hydroxy groups, and m is from 1 to 4, preferably from 2 to 3, more preferably 3, with no more than one hydroxy group in any (C(R_b)₂) moiety.

[0089] Preferred R_2 is hydrogen, or a C_1 - C_3 alkyl and more preferably methyl. Preferred R_3 is C_1 - C_4 sulphonate group, or a C_1 - C_3 alkyl and more preferably methyl. Preferred R_4 is $(CH_2)_n$ wherein n is an integer from 1 to 10, preferably from 1 to 6, more preferably is from 1 to 3.

[0090] Some common examples of betaine/sulphobetaine are described in U.S. Pat. Nos. 2,082,275, 2,702,279 and 2,255,082.

[0091] Examples of particularly suitable alkyldimethyl betaines include coconut-dimethyl betaine, lauryl dimethyl betaine, decyl dimethyl betaine, 2-(N-decyl-N, N-dimethyl-ammonia)acetate, 2-(N-coco N, N-dimethylammonio) acetate, myristyl dimethyl betaine, palmityl dimethyl betaine, cetyl dimethyl betaine, stearyl dimethyl betaine. For example Coconut dimethyl betaine is commercially available from Seppic under the trade name of Amonyl 265[®]. Lauryl betaine is commercially available from the trade name Empigen BB/L[®].

[0092] Examples of amidobetaines include cocoamidoethylbetaine, cocoamidopropyl betaine or C_{10} - C_{14} fatty acylamidopropylene(hydropropylene)sulfobetaine. For example C_{10} - C_{14} fatty acylamidopropylene(hydropropylene)sulfobetaine is commercially available from Sherex Company under the trade name "Varion CAS® sulfobetaine".

[0093] A further example of betaine is Lauryl-immino-dipropionate commercially available from Rhone-Poulenc under the trade name Mirataine H_2C -HA®.

[0094] Suitable anionic surfactants to be used in the compositions herein include water-soluble salts or acids of the formula $ROSO_3M$ wherein R preferably is a C_{10} - C_{24} hydrocarbyl, preferably an alkyl or hydroxyalkyl having a C_{10} - C_{20} alkyl component, more preferably a C_{12} - C_{18} alkyl or hydroxyalkyl, and M is H or a cation, e.g., an alkali metal cation (e.g., sodium, potassium, lithium), or ammonium or substituted ammonium (e.g., methyl-, dimethyl-, and trimethyl am-

20 monium cations and quaternary ammonium cations, such as tetramethyl-ammonium and dimethyl piperdinium cations and quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like). Typically, alkyl chains of C₁₂₋₁₆ are preferred for lower wash temperatures (e.g., below about 50°C) and C₁₆₋₁₈ 8 alkyl chains are preferred for higher wash temperatures (e.g., above about 50°C). [0095] Other suitable anionic surfactants for use herein are water-soluble salts or acids of the formula RO(A)_mSO₃M

wherein R is an unsubstituted C_{10} - C_{24} alkyl or hydroxyalkyl group having a C_{10} - C_{24} alkyl component, preferably a C_{12} - C_{20} alkyl or hydroxyalkyl, more preferably C_{12} - C_{18} alkyl or hydroxyalkyl, A is an ethoxy or propoxy unit, m is greater than zero, typically between 0.5 and 6, more preferably between 0.5 and 3, and M is H or a cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, calcium, magnesium, etc.), ammonium or substituted-ammonium cation. Alkyl ethoxylated sulfates as well as alkyl propoxylated sulfates are contemplated herein. Specific examples

of substituted ammonium cations include methyl-, dimethyl-, trimethyl-ammonium and quaternary ammonium cations, such as tetramethyl-ammonium, dimethyl piperdinium and cations derived from alkanolamines such as ethylamine, diethylamine, triethylamine, mixtures thereof, and the like. Exemplary surfactants are C₁₂-C₁₈ alkyl polyethoxylate (1.0) sulfate (C₁₂-C₁₈E(1.0)SM), C₁₂-C₁₈ alkyl polyethoxylate (2.25) sulfate (C₁₂-C₁₈E(2.25)SM), C₁₂-C₁₈ alkyl polyethoxylate (3.0) sulfate (C₁₂-C₁₈E(3.0)SM), and C₁₂-C₁₈ alkyl polyethoxylate (4.0) sulfate (C₁₂-C₁₈E(4.0)SM), wherein M is conveniently selected from sodium and potassium.

[0096] Other anionic surfactants useful for detersive purposes can also be used herein. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of soap, C_9 - C_{20} linear alkylbenzenesulphonates, C_8 - C_{22} primary or secondary alkanesulphonates, C_8 - C_{24} olefinsulphonates, sulphonated polycarboxylic acids prepared by sulphonation of the pyrolyzed product of alkaline

40 earth metal citrates, e.g., as described in British patent specification No. 1,082,179, C₈-C₂₄ alkylpolyglycolethersulfates (containing up to 10 moles of ethylene oxide); alkyl ester sulphonates such as C₁₄₋₁₆ methyl ester sulphonates; acyl glycerol sulphonates, fatty oleyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, paraffin sulphonates, alkyl phosphates, isethionates such as the acyl isethionates, N-acyl taurates, alkyl succinamates and sulfosuccinate, monoesters of sulfosuccinate (especially saturated and unsaturated C₁₂-C₁₈ monoesters) diesters of sulfosuccinate (especially saturated and unsaturated C₁₂-C₁₈ monoesters)

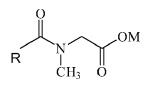
⁴⁵ pecially saturated and unsaturated C₆-C₁₄ diesters), sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described below), branched primary alkyl sulfates, alkyl polyethoxy carboxylates such as those of the formula RO(CH₂CH₂O)_kCH₂COO-M⁺ wherein R is a C₈-C₂₂ alkyl, k is an integer from 0 to 10, and M is a soluble salt-forming cation. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tall oil. Further

⁵⁰ examples are given in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A variety of such surfactants are also generally disclosed in U.S. Patent 3,929,678, issued December 30, 1975, to Laughlin, et al. at Column 23, line 58 through Column 29, line 23 (herein incorporated by reference).

[0097] Other suitable anionic surfactants to be used herein also include acyl sarcosinate or mixtures thereof, in its acid and/or salt form, preferably long chain acyl sarcosinates having the following formula:

55

5



5

10

wherein M is hydrogen or a cationic moiety and wherein R is an alkyl group of from 11 to 15 carbon atoms, preferably of from 11 to 13 carbon atoms. Preferred M are hydrogen and alkali metal salts, especially sodium and potassium. Said acyl sarcosinate surfactants are derived from natural fatty acids and the amino-acid sarcosine (N-methyl glycine). They are suitable to be used as aqueous solution of their salt or in their acidic form as powder. Being derivatives of natural fatty acids, said acyl sarcosinates are rapidly and completely biodegradable and have good skin compatibility.

[0098] Accordingly, suitable long chain acyl sarcosinates to be used herein include C₁₂ acyl sarcosinate (i.e., an acyl

- sarcosinate according to the above formula wherein M is hydrogen and R is an alkyl group of 11 carbon atoms) and
 ¹⁵ C14 acyl sarcosinate (i.e., an acyl sarcosinate according to the above formula wherein M is hydrogen and R is an alkyl group of 13 carbon atoms). C₁₂ acyl sarcosinate is commercially available, for example, as Hamposyl L-30® supplied by Hampshire. C₁₄ acyl sarcosinate is commercially available, for example, as Hamposyl M-30® supplied by Hampshire.
 [0099] Suitable amphoteric surfactants to be used herein include amine oxides having the following formula R₁R₂R₃NO wherein each of R₁, R₂ and R₃ is independently a saturated substituted or unsubstituted, linear or branched hydrocarbon
- 20 chains of from 1 to 30 carbon atoms. Preferred amine oxide surfactants to be used are amine oxides having the following formula R₁R₂R₃NO wherein R₁ is an hydrocarbon chain comprising from 1 to 30 carbon atoms, preferably from 6 to 20, more preferably from 8 to 16, most preferably from 8 to 12, and wherein R₂ and R₃ are independently substituted or unsubstituted, linear or branched hydrocarbon chains comprising from 1 to 4 carbon atoms, preferably from 1 to 3 carbon atoms, and more preferably are methyl groups. R1 may be a saturated substituted or unsubstituted linear or branched
- ²⁵ hydrocarbon chain. Suitable amine oxides for use herein are for instance natural blend C_8-C_{10} amine oxides as well as $C_{12}-C_{16}$ amine oxides commercially available from Hoechst.

Chelating agents:

- ³⁰ **[0100]** The compositions may comprise a chelating agent as a preferred optional ingredient. Suitable chelating agents may be any of those known to those skilled in the art such as the ones selected from the group comprising phosphonate chelating agents, amino carboxylate chelating agents, other carboxylate chelating agents, polyfunctionally-substituted aromatic chelating agents, ethylenediamine N,N'- disuccinic acids, or mixtures thereof.
- **[0101]** A chelating agent may be desired in the compositions as it allows to increase the ionic strength of the compositions herein and thus their stain removal and bleaching performance on various surfaces. The presence of chelating agents may also contribute to reduce the tensile strength loss of fabrics and/or color damage, especially in a laundry pretreatment application.

[0102] Suitable phosphonate chelating agents to be used herein may include alkali metal ethane 1-hydroxy diphosphonates (HEDP), alkylene poly (alkylene phosphonate), as well as amino phosphonate compounds, including amino

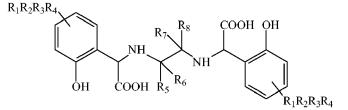
- ⁴⁰ aminotri(methylene phosphonic acid) (ATMP), nitrilo trimethylene phosphonates (NTP), ethylene diamine tetra methylene phosphonates, and diethylene triamine penta methylene phosphonates (DTPMP). The phosphonate compounds may be present either in their acid form or as salts of different cations on some or all of their acid functionalities. Preferred phosphonate chelating agents to be used herein are diethylene triamine penta methylene phosphonate (DTPMP) and ethane 1-hydroxy diphosphonate (HEDP). Such phosphonate chelating agents are commercially available from Mon-
- santo under the trade name DEQUEST®.
 [0103] Polyfunctionally-substituted aromatic chelating agents may also be useful in the compositions herein. See U.S. patent 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are dihydroxy-disulfobenzenes such as 1,2-dihydroxy -3,5-disulfobenzene.
- [0104] A preferred biodegradable chelating agent for use herein is ethylene diamine N,N'-disuccinic acid, or alkali metal, or alkaline earth, ammonium or substitutes ammonium salts thereof or mixtures thereof. Ethylenediamine N,N'disuccinic acids, especially the (S,S) isomer, have been extensively described in US patent 4, 704, 233, November 3, 1987, to Hartman and Perkins. Ethylenediamine N,N'- disuccinic acid is, for instance, commercially available under the tradename ssEDDS® from Palmer Research Laboratories.
- [0105] Suitable amino carboxylates to be used herein include ethylene diamine tetra acetates, diethylene triamine pentaacetates, diethylene triamine pentaacetate (DTPA),N-hydroxyethylethylenediamine triacetates, nitrilotri-acetates, ethylenediamine tetrapropionates, triethylenetetraaminehexa-acetates, ethanol-diglycines, propylene diamine tetracetic acid (PDTA) and methyl glycine di-acetic acid (MGDA), both in their acid form, or in their alkali metal, ammonium, and substituted ammonium salt forms. Particularly suitable amino carboxylates to be used herein are diethylene triamine

penta acetic acid, propylene diamine tetracetic acid (PDTA) which is, for instance, commercially available from BASF under the trade name Trilon FS® and methyl glycine di-acetic acid (MGDA).

[0106] Further carboxylate chelating agents to be used herein include salicylic acid, aspartic acid, glutamic acid, glycine, malonic acid or mixtures thereof.

5 [0107] Another chelating agent for use herein is of the formula:





15

20

wherein R₁, R₂, R₃, and R₄ are independently selected from the group consisting of-H, alkyl, alkoxy, aryl, aryloxy, -Cl, -Br, -NO₂, -C(O)R', and -SO₂R"; wherein R' is selected from the group consisting of -H, -OH, alkyl, alkoxy, aryl, and aryloxy; R" is selected from the group consisting of alkyl, alkoxy, aryl, and aryloxy; and R₅, R₆, R₇, and R₈ are independently selected from the group consisting of -H and alkyl.

[0108] Particularly preferred chelating agents to be used herein are amino aminotri(methylene phosphonic acid), diethylene-triamino-pentaacetic acid, diethylene triamine penta methylene phosphonate, 1-hydroxy ethane diphosphonate, ethylenediamine N, N'-disuccinic acid, and mixtures thereof.

[0109] Typically, the compositions may comprise up to 5%, preferably from 0.01% to 1.5% by weight and more preferably from 0.01% to 0.5% by weight of the total composition of a chelating agent.

Radical scavenger:

[0110] The compositions may comprise a radical scavenger or a mixture thereof. Suitable radical scavengers for use herein include the well-known substituted mono and dihydroxy benzenes and their analogs, alkyl and aryl carboxylates and mixtures thereof. Preferred such radical scavengers for use herein include di-tert-butyl hydroxy toluene (BHT), hydroquinone, di-tert-butyl hydroquinone, mono-tert-butyl hydroquinone, tert-butyl-hydroxy anysole, benzoic acid, toluic acid, catechol, t-butyl catechol, benzylamine, 1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl) butane, n-propyl-gallate or mixtures thereof and highly preferred is di-tert-butyl hydroxy toluene. Such radical scavengers like N-propyl-gallate may

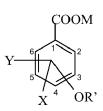
³⁵ be commercially available from Nipa Laboratories under the trade name Nipanox S1 ®. Radical scavengers when used, are typically present herein in amounts ranging from up to 10% and preferably from 0.001% to 0.5% by weight of the total composition.

[0111] The compositions according to the present invention, may comprise as a highly preferred, but optional ingredient an alkoxylated benzoic acid or a salt thereof.

⁴⁰ **[0112]** Indeed, the composition, containing chlorine dioxide and alkoxylated benzoic acid or a salt thereof, provides excellent stain removal performance and, in the same time, provides color safety.

[0113] Generally, the alkoxylated benzoic acid or the salt thereof has the general formula :

45



50

55

wherein : the substituents of the benzene ring X and Y are independently selected from - H, or -OR'; R' is independently selected from C1 to C20 linear or branched alkyl chains, preferably R' is independently selected from C1 to C5 linear or branched alkyl chains, more preferably R' is -CH3, and; M is hydrogen, a cation or a cationic moiety. Preferably, M is selected from the group consisting of hydrogen, alkali metal ions and alkaline earth metal ions. More preferably, M is explored from the group consisting of hydrogen, action or preferably. M is hydrogen, and preferably and preferably. M is hydrogen, and alkaline earth metal ions. More preferably, M is explored from the group consisting of hydrogen, and preferably and preferably.

selected from the group consisting of hydrogen, sodium and potassium. Even more preferably, M is hydrogen. [0114] Preferably, said alkoxylated benzoic acid or a salt thereof, is selected from the group consisting of : a monoalkoxy benzoic acid, or a salt thereof, a dialkoxy benzoic acid, or a salt thereof; a trialkoxy benzoic acid, or a salt thereof; and

a mixture thereof. More preferably, said alkoxylated benzoic acid or a salt thereof, is selected from the group consisting of : a dialkoxy benzoic acid, or a salt thereof; a trialkoxy benzoic acid, or a salt thereof; and a mixture thereof. Even more preferably, said alkoxylated benzoic acid or a salt thereof, is a trimethoxy benzoic acid or a salt thereof.

[0115] In a highly preferred embodiment of the present invention, said alkoxylated benzoic acid or the salt thereof is a trimethoxy benzoic acid or a salt thereof (TMBA), wherein in the above general formula : the substituents of the benzene ring Y and X are -OR'; R' is - CH3 and; M is hydrogen, a cation or a cationic moiety.

[0116] Typically, the bleaching composition according to the present invention may comprise from 0.001% to 5%, preferably from 0.005% to 2.5% and more preferably from 0.01% to 1.0% by weight of the total composition of said alkoxylated benzoic acid or a salt thereof.

10

15

5

Antioxidant :

[0117] The compositions may further comprise an antioxidant or mixtures thereof. Typically, the compositions herein may comprise up to 10%, preferably from 0.002% to 5%, more preferably from 0.005% to 2%, and most preferably from 0.01 % to 1% by weight of the total composition of an antioxidant.

[0118] Suitable antioxidants to be used herein include organic acids like citric acid, ascorbic acid, tartaric acid, adipic acid and sorbic acid, or amines like lecithin, or aminoacids like glutamine, methionine and cysteine, or esters like ascorbil palmitate, ascorbil stearate and triethylcitrate, or mixtures thereof. Preferred antioxidants for use herein are citric acid, ascorbic acid, ascorbil palmitate, lecithin or mixtures thereof.

20 Builder :

[0119] The compositions may further comprise one or more builders and/or a modified polycarboxylate co-builder.

[0120] Suitable builders are selected from the group consisting of : organic acids and salts thereof; polycarboxylates; and mixtures thereof. Typically said builders have a calcium chelating constant (pKCa) of at least 3. Herein the pKCa the value of a builder or a mixture thereof is measured using a 0.1M NH₄Cl-NH₄OH buffer (pH 10 at 25°C) and a 0.1% solution of said builder or mixture thereof with a standard calcium ion electrode.

[0121] Examples of builders are organic acids like citric acid, lactic acid, tartaric acid, oxalic acid, malic acid, monosuccinic acid, disuccinic acid, oxydisuccinic acid, carboxymethyl oxysuccinic acid, diglycolic acid, carboxymethyl tartronate, ditartronate and other organic acid or mixtures thereof.

[0122] Suitable salts of organic acids include alkaline, preferably sodium or potassium, alkaline earth metal, ammonium or alkanolamine salts.

[0123] Such organic acids and the salts thereof are commercially available from Jungbunzlaur, Haarman & Reimen, Sigma-Aldrich or Fluka.

- ³⁵ **[0124]** Other suitable builders include a wide variety of polycarboxylate compounds. As used herein, "polycarboxylate" refers to compounds having a plurality of carboxylate groups, preferably at least 3 carboxylates. Polycarboxylate builder can generally be added to the composition in acid form, but can also be added in the form of a neutralized salt or "overbased". When utilized in salt form, alkali metals, such as sodium, potassium, and lithium, or alkanolammonium salts are preferred.
- 40 [0125] Useful polycarboxylates include homopolymers of acrylic acid and copolymers of acrylic acid and maleic acid. [0126] Other useful polycarboxylate builders include the ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1,3,5-trihydroxy benzene-2,4,6-trisulfonic acid, and carboxymethyloxysuccinic acid, the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as nitrilotriacetic acid, as well as polycarboxylates such as mellitic acid, succinic acid, oxydisuccinic acid, polymaleic acid, benzene 1,3,5-
- 45 tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.
 [0127] Suitable polycarboxylates are commercially available from Rohm & Haas under the trade name Norasol® or Acusol®.

[0128] Preferred builders herein are selected from the group consisting of : citric acid; tartaric acid; tartrate monosuccinate; tartrate disuccinate; lactic acid; oxalic acid; and malic acid; and mixtures thereof. Even more preferred builders

- ⁵⁰ herein are selected from the group consisting of : citric acid; tartaric acid; tartrate monosuccinate; tartrate disuccinate; and malic acid; and mixtures thereof. The most preferred builders herein are selected from the group consisting of : citric acid; tartratic acid; tartrate monosuccinate; and tartrate disuccinate; and mixtures thereof.
 [0129] Typically the bleaching compositions herein may comprise up to 40%, preferably from 0.01% to 25%, more
- preferably from 0.1% to 15%, and most preferably from 0.5% to 10% by weight of the total composition of said builder.
 [0130] The compositions may further comprise a modified polycarboxylate co-builder. The term "polycarboxylate" refers to compounds having a plurality of carboxylate groups, preferably at least 3 carboxylates.

[0131] By "modified polycarboxylate" it is meant herein that at least at one end of the polycarboxylate compound, i.e., the polycarboxylate chain, said compound is modified by a functional group, e.g., a phosphono group.

[0132] Preferred modified polycarboxylate co-builders are polycarboxylates with phosphono end groups.

- [0133] By "phosphono end group" it is meant herein a phosphono functional group according to the formula:
- 5

5

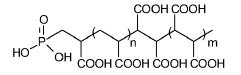


10

wherein each M is independently H or a cation, preferably both M are H.
[0134] Examples of suitable polycarboxylates with phosphono end groups are copolymers of acrylic acid and maleic acid having a phosphono end group and homopolymers of acrylic acid having a phosphono end group.
[0135] A preferred modified polycarboxylate is a copolymer of acrylic acid and maleic acid with a phosphonic/phospho-

¹⁵ no end group according to the general formula :

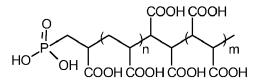
20



- having an average molecular weight of from 1000 to 100000, preferably an average molecular weight of from 1000 to
 20000, more preferably an average molecular weight of from 1000 to 10000, and most preferably an average molecular weight of from 1500 to 5000; wherein n is from 10 mol% to 90 mol%, preferably 80 mol% and m is from 10 mol% to 90 mol%, preferably 20 mol%.
 - **[0136]** Accordingly, an example of a suitable modified polycarboxylate is a copolymer of acrylic acid and maleic acid (80/20) with a phosphonic/phosphono end group according to the formula:

30

35



wherein n is 80 mol% and m is 20 mol%; having an average molecular weight of 2000.

⁴⁰ **[0137]** Such modified polycarboxylate are available from Rohm & Haas under the trade name Acusol 425®, Acusol 420® or Acusol 470®.

[0138] Typically the bleaching compositions herein may comprise up to 40%, preferably from 0.01% to 25%, more preferably from 0.1% to 15%, and most preferably from 0.5% to 5% by weight of the total composition of said modified polycarboxylate co-builder.

45

Anti-resoiling polymers:

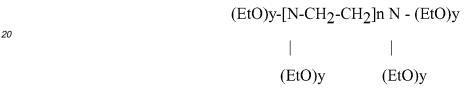
[0139] The compositions may comprise as a highly preferred, but optional ingredient an anti-resoiling polymer.

[0140] Suitable anti-resoiling polymers include soil suspending polyamine polymers. Any soil suspending polyamine polymer known to those skilled in the art may also be used herein. Particularly suitable polyamine polymers for use herein are alkoxylated polyamines. Such materials can conveniently be represented as molecules of the empirical structures with repeating units :

	[N - R]n Ama	ine form	and	R1 - [N+ - R]n	nX⁻	Quaternized form
5						
	(alkoxy)y			(alkoxy)y		

10 wherein R is a hydrocarbyl group, usually of 2-6 carbon atoms; R₁ may be a C₁-C₂₀ hydrocarbon; the alkoxy groups are ethoxy, propoxy, and the like, and y is from 2 to 30, most preferably from 7 to 20; n is an integer of at least 2, preferably from 2 to 40, most preferably from 2 to 5; and X- is an anion such as halide or methylsulfate, resulting from the guaternization reaction.

[0141] Highly preferred polyamines for use herein are the so-called ethoxylated polyethylene amines, i.e., the polym-15 erized reaction product of ethylene oxide with ethyleneimine, having the general formula :



25

30

5

wherein y is from 2 to 50, preferably from 5 to 30, and n is from 1 to 40, preferably from 2 to 40. Particularly preferred for use herein is an ethoxylated polyethylene amine, in particular an ethoxylated polyethylene amine wherein n=2 and y=20, and an ethoxylated polyethylene amine wherein n=40 and y=7.

[0142] Suitable ethoxylated polyethylene amines are commercially available from Nippon Shokubai CO., LTD or from BASF.

[0143] Furthermore, highly preferred polyamines for use herein are the so-called ethoxylated polyethylene guaternized amines having the general formula :

 $\begin{array}{c} R_1 \\ | \\ \end{array}$ R_1 35 (EtO)y - $[N^+ - CH_2 - CH_2] n - N^+$ (EtO)y | (EtO)y (EtO)y

40

50

45 wherein y is from 2 to 50, preferably from 5 to 30, and n is from 1 to 40, preferably from 2 to 40 and R1 and R2 are independently a C1-C20 hydrocarbon. Particularly preferred for use herein is an ethoxylated polyethylene amine, in particular an ethoxylated polyethylene amine wherein n=2 and y=20, and an ethoxylated polyethylene amine wherein n=40 and y=7.

[0144] Particularly preferred herein is 24-Ethoxylated Hexamethylene Diamine Quaternized methyl chloride (EHDQ), commercially available from BASF.

[0145] The invention is further illustrated by the following examples. The following examples are meant to exemplify compositions used in process according to the present invention but are not necessarily used to limit or otherwise define the scope of the present invention.

55 Example 1 : Compositions

[0146] The compositions are made by combining the listed ingredients in the listed proportions (weight % unless otherwise specified).

Composition	i	ii	
Carnebon 200 (1)	86.600	84.600	
H ₂ O ₂	-	2.000	
Marlipal 24.7 (2)	2.500	2.500	
Neodol 23-1.1E (3)	2.500	2.500	
КОН	1.400	1.400	
HLAS (6)	5.000	5.000	
HEDP (7)	1.000	1.000	
Perfume	0.130	0.130	

[0147] Compositions I-XII are packaged in a two compartments container wherein a first compartment comprises compositions A, comprising a chlorine dioxide precursor, and wherein a second compartment comprises compositions B, comprising a chlorine dioxide activator.

20	Composition A	I	II	III	IV
	NaClO ₂	0.800	0.800	0.800	0.800
	Hydrogen Peroxide	-	-	2.000	-
	Marlipal 24.7 (2)	-	-	2.460	2.460
25	Neodol 23-1.1E (3)	-	-	2.495	2.495
	КОН	-	-	1.360	1.360
	HLAS (6)	-	-	4.950	4.950
	HEDP (7)	-	-	1.000	1.000
0	Perfume	-	-	0.130	0.130
U	TMBA (5)	-	-	0.030	0.030
	Water and minors		up to	100%	
5	Composition B	I	II	111	IV
5	Hydrogen Peroxide	2.000	2.000	-	2.000
	Citric acid	3.200	-	3.200	3.200
	Marlipal 24.7 (2)	2.460	2.460	-	2.460
	Neodo123-1.1E (3)	2.495	2.495	-	2.495
0	КОН	1.360	1.360	-	1.360
	HLAS (6)	4.950	4.950	-	4.950
	HEDP (7)	1.000	1.000	-	1.000
	TMBA (5)	-	-	-	0.030
	Perfume	0.130	0.130	-	0.130
5	Water and minors		up to	100%	

	Composition A	V	VII	VII	VIII
50	NaClO ₂	0.800	1.000	2.000	2.000
	Hydrogen Peroxide	-	-	2.000	-
	Marlipal 24.7 (2)	2.500	-	2.500	2.500
	Neodol 23-1.1E (3)	2.500	-	2.500	2.500
55	HEDP (7)	-	-	1.000	1.000
	EHDQ (4)	-	-	2.000	-
	Na ₂ CO ₃	0.100	-	-	-

⁽continued)

	mposition A	V	/ V		VII	VII
Perfume		-	-		0.030	0.03
Water and m	ninors			- up to 100	%	
Co	mposition B	V	v v	11	VII	VIII
Hydrogen Pe	eroxide	2.0	- 00		-	2.00
Sodium pers	ulfate	6.0	00 5.0	00	6.000	6.00
Marlipal 24.7	(2) Neodol 23-1.1	E(3) 2.5	- 00		-	2.50
HEDP (7)		1.0	- 00		-	1.00
TMBA (5)		0.0	30 -		-	0.03
EHDQ (4)		2.0	- 00		-	-
Perfume		-	-		-	-
Water and m	ninors			up to 100	%	
	mposition A	IX	x	XI		KII
	-		^ 1.000			000
NaCl	ogen Peroxide	0.800	1.000	2.000		
-	•	-	-	2.000		- 500
	pal 24.7 9 (2)	2.500	-	2.500		
	dol 23-1.1E (3)	2.500	-	2.500		500
	P (7)	-	-	1.000	1.	000
	Q (4)	-	-	2.000		-
Na ₂ C	-	0.100	-	-		-
Perfu		-	-	0.030		030
Wate	er and minors		up to	100%		
	maccition D	IX	x	XI		/11
	mposition B					
-	ogen Peroxide	2.000	-	-		000
	um persulfate	6.000	5.000	6.000		000
	pal 24.7	2.500	-	-		500
	dol 23-1.1E	2.500	-	-		500
HED		1.000	-	-		000
	A (5)	0.030	-	-	0.0	030
		0 000	_	-		-
EHD		2.000	-			
EHD Wate	er and minors		up to			
EHD Wate (1) C	er and minors Carnebon 200 (ar	n aqueous cor	nposition of sta	abilized Ch		tide) is
EHD Wate (1) C comr	er and minors Carnebon 200 (ar mercially available	n aqueous cor e from Internat	nposition of stational Dioxcide I	abilized Ch nc.	lorine Diox	
EHD Wate (1) C comr (2) M	er and minors Carnebon 200 (ar mercially available Marlipal 24.7 (C12	n aqueous cor e from Internat	nposition of stational Dioxcide I	abilized Ch nc.	lorine Diox	
EHD Wate (1) C comr (2) M Conc	er and minors Carnebon 200 (ar mercially available Aarlipal 24.7 (C12 dea.	aqueous cor from Internat 2-14 ethoxylat	nposition of sta ional Dioxcide I ed alcohol) is	abilized Ch nc. commercia	llorine Diox	e from
EHD Wate (1) C comr (2) M Conc (3) N	er and minors Carnebon 200 (ar mercially available Marlipal 24.7 (C12 dea. leodol 23-1.1E (C	aqueous cor from Internat 2-14 ethoxylat	nposition of sta ional Dioxcide I ed alcohol) is	abilized Ch nc. commercia	llorine Diox	e from
EHD Wate (1) C comr (2) M Conc (3) N Shell	er and minors Carnebon 200 (ar mercially available Marlipal 24.7 (C12 dea. leodol 23-1.1E (C l.	n aqueous cor from Internat 2-14 ethoxylat 22-13 ethoxyla	nposition of sta ional Dioxcide I ed alcohol) is ated alcohol) is	abilized Ch nc. commercia commercia	llorine Diox	e from
EHD Wate (1) C comr (2) M Conc (3) N Shell (4) E	er and minors Carnebon 200 (ar mercially available Marlipal 24.7 (C12 dea. leodol 23-1.1E (C l. HDQ is Ethoxylate	aqueous cor from Internat 2-14 ethoxylat 212-13 ethoxylat	nposition of sta ional Dioxcide I ed alcohol) is ated alcohol) is lene diamine qu	abilized Ch nc. commercia commercia uatemized.	ilorine Diox Ily availabl ally availabl	e from le from
EHD Wate (1) C comr (2) M Conc (3) N Shell (4) E (5) T	er and minors Carnebon 200 (ar mercially available Aarlipal 24.7 (C12 dea. leodol 23-1.1E (C l. HDQ is Ethoxylat MBA (3,4,5-Trime	aqueous cor from Internat 2-14 ethoxylat 212-13 ethoxylat	nposition of sta ional Dioxcide I ed alcohol) is ated alcohol) is lene diamine qu	abilized Ch nc. commercia commercia uatemized.	ilorine Diox Ily availabl ally availabl	e from le from
EHD Wate (1) C comr (2) M Conc (3) N Shell (4) E (5) T Aldrid	er and minors Carnebon 200 (ar mercially available Aarlipal 24.7 (C12 dea. leodol 23-1.1E (C l. HDQ is Ethoxylat MBA (3,4,5-Trime	aqueous cor from Internat 2-14 ethoxylat 12-13 ethoxylat ed hexamethy thoxy benzene	nposition of sta ional Dioxcide I ed alcohol) is ated alcohol) is lene diamine qu sulfonic acid) is	abilized Ch nc. commercia commercia uatemized.	ilorine Diox Ily availabl ally availabl	e from le from

55

[0148] The above compositions i and ii are applied to the fabrics and are left in contact with fabrics during 10 minutes before said fabrics are washed.

[0149] The mixing of the composition A + composition B of compositions I to XII, are applied onto the fabrics with a

multi-compartments spray and are left in contact with the fabrics during 10 minutes before said fabrics are washed.

Example 2 : Efficiency test

5 I. Bleaching performance.

[0150] Several tests were performed, using a conventional method to measure bleaching efficiency. Particularly, tests were performed by using chlorine dioxide as a pretreater and compare for pretreatment with conventional bleaches such as hypochlorite bleach. The test procedure is performed by the following process:

10

15

- Standards Stain fabrics swatches ("Standard Equest Set Stain" from Equest) are pretreated either by applying 1 ml of the composition A+ B of composition II of Example 1 with a two-compartments bottle, or by applying 1 ml of a conventional hydrogen peroxide pretreater (Ace Oxi®) on fabrics and left onto during 10 minutes;
- Fabrics are loaded into a regular Miele® or Bauknecht® washing machine;
- Wash is performed at 40°C with a detergent (Dash Powder®), under a short wash cycle (around 80 min);
- Optionally, hypochlorite bleach (Ace®) is added in the 2nd rinse of the wash.
- Bleaching performances are compared by an image analyses (Laundry Image Analysis system) by comparing the soiled fabrics treated with the composition of the present invention with those treated with the conventional bleach).
- 20 [0151] The Laundry Image Analysis system measures stain removal on technical stain swatches. The system utilizes a video camera to acquire color images of swatches. An image of the swatch is taken both before and after it is washed. The acquired image is then analyzed by computer software (Global R&D Computing). The software compares the unwashed stain to the washed stain, as well as the unwashed fabric to the washed fabric and produces five figures of merit which describe stain removal. The data are then analyzed by a Statistical Analysis program to determine statistically significant differences between the treatments.

[0152] The result is express within a percentage of a stain removal index. The stain removal index uses the initial fabric as the reference against which to measure color differences between unwashed and washed stain. A higher value indicates a better bleach performance. All the results are statistically significant.

30	Stain removal index (%)		Detergent Alone	CIO ₂ pretreater, then wash with detergent	Increasing performances %
	Food Stains :	Spinach	83	94	+ 11
35		β-carotene	63	97	+ 24
		Ragu	56	95	+ 39
		Curry	62	93	+ 31

40

40	Stain removal	tain removal index (%) rinse)		CIO ₂ pretreater, then wash with detergent	Increasingperformances %	
45	Food Stains :	Spinach	89	93	+4	
45		Ragu	86	94	+ 8	
		Curry	84	94	+ 10	
	Beverages :	Red Wine	89	95	+ 7	
50		Coffee	93	96	+ 3	
	Outdoor :	Clay	50	64	+ 14	

Stain removal index (%)	H ₂ O ₂ pretreater, then wash with detergent	CIO ₂ pretreater, then wash with detergent	Increasing performances %
Food Stains : Ragu	45	95	+ 50

(continued)

Stair			CIO ₂ pretreater, then wash with detergent	Increasing performances %
	β-carotene	56	95	+ 39
	Curry	53	88	+ 35
	Spinach	84	92	+ 8
Bevera	ages	87	93	+ 6
Greas	y	84	89	+ 5
Outdo	or: Clay	71	72	+ 1
Cosme	etics	45	48	+ 3

15

20

25

II. Colour safety efficiency:

[0153] Several tests were performed, using conventional methods to measure colour safety efficiency. Particularly, tests were made by using chlorine dioxide as a pretreater and by comparison with conventional hypochlorite bleaches. The test procedure is performed by the fallowing process:

- Standard fabrics swatches dyes are prepared using the standard dyed fabrics ("AISE 41 Dye Set");
- Fabrics are pretreated: 0.5 ml of an aqueous composition containing 1.90% of Citric acid and 0.76% of NaClO₂, or of a conventional hypochlorite bleach (Ace®), are applied in-situ on the standard dyed fabrics during 10 minutes.
- The fabrics are washed immediately after the pretreatment time.
 - Fabrics are loaded into a regular Miele® or Bauknecht® washing machine;
- A wash at 40°C is made (on "normal" wash condition for color care) with a classic detergent (Dash Powder®) under a short wash cycle (around 80 min);
- The evaluation is made visually by at least two judges in a panel. Grading is versus an untreated, but washed 30 reference.

[0154] A fail in the result is considered when the color damage is noticeable on inspection or when the affected area is noticeably lighter shade than untreated area, or when the color is almost completely removed.

Dye class:	Number of samples in class	Number of Fails		
		Hypochlorite	CIO ₂	
Reactive	14	14	0	
Direct	8	5	0	
Disperse	5	1	0	
Basic	2	0	0	
Acid	6	0	0	
Total	35	20	0	

35

40

45

[0155] Theses results clearly shows that the use of chlorine dioxide improve the color safety of dyes by comparison with hypochlorite.

50

III. Colour safety efficiency:

55

[0156] Several tests were performed, using conventional methods to measure colour safety efficiency. Particularly, tests were made by using chlorine dioxide as a pretreater and by comparison with composition containing chlorine dioxide and other compounds such as Succinic acid; radical scavenger (TMBA); chlorine scavengers (Monoethanolamine MEA); dye maintenance agent (epi-chlorohydrin copolymer).

[0157] This test were analysed by comparison with a "worst case reference" pure CIO₂ (How-High-Is-Up prototype).

[0158] Dyes (from the 41 AISE dye set) are treated with a total of 1ml pretreater for 10 minutes and for 24 hours then washed with HDL under usage instruction at 40 °C. Set Grading is made versus the untreated area of a dyed fabric. The scale (from 0 to 4) for evaluation of color damage is:

0 - No damage

- 1 Slight damage (only noticeable in "correct light" if inspecting closely).
- 2 Small amount of damage (noticeable on inspection only).
- 3 Medium amount of damage (affected area is noticeably lighter shade than untreated area).
- 4 Heavy damage (color is almost completely removed).

10

5

dye evaluated after 10 min.	worst case reference : CIO ₂ alone	CIO ₂ + Succinic acid	CIO ₂ + TMBA	CIO ₂ + MEA	CIO ₂ + epichlorohy. copol.
Vat Blue	4	4	4	3	0
Reactive violet	2	0	0	0	0

20

25

15

dye evaluated after 24 hours.	worst case reference : CIO ₂ alone	CIO ₂ + Succinic acid	CIO ₂ + TMBA	CIO ₂ + MEA
Reactive Yellow	3	2	3	0
Reactive violet	3	2	2	2

[0159] Theses results clearly shows that the use of chlorine dioxide in combination with other specific compound improve the color safety on specific dyes by comparison with the use of CIO2 alone.

³⁰ **[0160]** The dimensions and values disclosed herein are not to be understood as being strictly limited to the exact numerical values recited. Instead, unless otherwise specified, each such dimension is intended to mean both the recited value and a functionally equivalent range surrounding that value. For example, a dimension disclosed as "40 mm" is intended to mean "about 40 mm".

35 Claims

1. A process of pretreating a fabric which comprises the steps of applying a liquid bleaching composition in its neat form onto said fabric and allowing said composition to remain in contact with said fabric for an effective amount of time before said fabric is washed and/or rinsed, **characterized in that** the composition comprises chlorine dioxide.

- 2. The process according to claim 1 wherein the composition comprises from 0.0001% to 10% by weight of the total composition of chlorine dioxide, preferably from 0.001 % to 2% by weight and more preferably from 0.01 % to 0.5%.
- ⁴⁵ **3.** The process according to any of the preceding claims wherein the composition comprises chlorine dioxide and peroxygen bleach.
 - **4.** The process according to claim 3 wherein the peroxygen bleach is hydrogen peroxide or a water soluble source thereof, preferably hydrogen peroxide.
- 50 5. The process according to any of the claims 3 or 4 wherein said composition comprises from 0.01% to 20% by weight of the total composition of said peroxygen bleach or mixtures thereof, preferably from 0.1 % to 10% and more preferably from 1% to 7%.
- **6.** The process according to any of the preceding claims wherein said composition further comprises surfactants and/or polymers.
 - 7. The process according to any of the preceding claims wherein said composition further comprises dye maintenance

agent.

- 8. The process according to claim 7 wherein said dye maintenance agent is a cyclic amine based polymer, oligomer or copolymer, preferably is an imidazole.
- 5
- **9.** The process according to any of the preceding claims wherein said composition further comprises a chlorine scavengers, preferably selected from the group consisting of monoethanolamine.
- 10. The process according to any of the preceding claims wherein the composition is packaged in a multi-compartment container having at least two compartments, wherein a first compartment contains a composition comprising a chlorine dioxide precursor and wherein a second compartment contains a composition comprising a chlorine dioxide activator.
- 11. The Process according to claim 10 wherein the chlorine dioxide precursor of the composition is chosen from the group consisting of sodium chlorite (NaClO₂), sodium chlorate (NaClO₃), potassium chlorite (KClO₂) potassium chlorate (KClO₃), lithium chlorate (LiClO₂), lithium chlorate (LiClO₃), chlorous acid (HClO₂) or chloric acid (HClO₃).
 - **12.** The Process according to claim 11 wherein the chlorine dioxide precursor is sodium chlorite or sodium chlorate, preferably sodium chlorite.
- 20
- **13.** The Process according to claim 11 or 12 wherein the chlorine dioxide precursor of the composition, in the first compartment, is comprised from 0.005% to 10% by weight of the total composition, preferably from 0.01% to 5% by weight and more preferably from 1% to 3%.
- 14. The Process according to any of claims 10 to 13 wherein the composition in the first compartment, comprising a chlorine dioxide precursor, has a pH equal or above 7.
 - **15.** The Process according to any of claims 10 to 13 wherein the composition in the second compartment, comprising a chlorine dioxide activator, has a pH below 7, preferably from 1 to 5 and more preferably from 3 to 5.
- 30
- **16.** The Process according to any of claims 10 to 14 wherein the chlorine dioxide activator of the composition is a source of acidity or an acid.
- **17.** The Process according to claim 15 wherein the chlorine dioxide activator of the composition is citric acid or oxalic acid, preferably citric acid.
 - **18.** The Process according to claim 15 wherein the chlorine dioxide activator of the composition is succinic acid.
- 19. Use of a composition comprising chlorine dioxide in laundry pretreatment.
- 40

35

- **20.** Use according to claim 19 wherein the composition is packaged in a multi-compartment container having at least two compartments, wherein a first compartment contains a composition comprising a chlorine dioxide precursor and wherein a second compartment contains a composition comprising a chlorine dioxide activator.
- 45 **21.** Use of a composition according to claims 19 or 20 to provide good bleaching performance and/or to provide color safety efficiency during pretreatment of fabrics.

50

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- WO 2005035708 A [0010]
- JP 59157375 A [0011]
- WO 9914301 A [0061]
- WO 0056849 A [0061]
- GB 809060 A, Thomas Hedley & Co., Ltd. [0086]
- US 2965576 A, E.R. Wilson [0086]
- US 2703798 A, Anthony M. Schwartz [0086]
- US 1985424 A, Piggott [0086]

- WO 9206070 A [0086]
- US 2082275 A [0090]
- US 2702279 A [0090]
- US 2255082 A [0090]
- GB 1082179 A [0096]
- US 3929678 A, Laughlin [0096]
- US 3812044 A, Connor [0103]
- US 4704233 A, Hartman and Perkins [0104]