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(54) Bleaching compositions

(57) The present invention relates to a bleaching composition comprising a preformed peroxy carboxylic acid and a metal phthalocyanine colouring agent wherein both the preformed peroxy acid and the colouring agent are storage stable in liquid conditions.

EP 1 065 263 A1

Description

Technical field

[0001] The present invention relates to a bleaching composition comprising a preformed peroxy carboxylic acid and a metal phthalocyanine colouring agent which is suitable to be used to bleach fabrics, clothes, carpets and the like.

Background of the invention

[0002] Commonly encountered liquid aqueous bleaching compositions suitable for the bleaching of stains on fabrics and hard-surfaces are based on halogen bleaches, especially hypochlorite bleaches. Halogen bleaches are extremely effective bleaching agents, however they also present a number of drawbacks which can sometimes dissuade a consumer from choosing the halogen-containing product. For example halogen bleaches, especially chlorine bleaches, emit a pungent odour during and after use (e.g., on consumer hands and/or surfaces treated therewith) which some consumers find disagreeable.

[0003] Furthermore, it is known in the art that halogen bleach-containing compositions (typically hypochlorite) are relatively aggressive to fabrics and may cause damage when used in relatively high concentration and/or repeated usage. In particular the consumer may perceive damage to the fabric itself (e.g. loss of tensile strength) or damage to the colour intensity of the fabric. While colour and fabric damage may be minimised by employing milder oxygen bleaches such as hydrogen peroxide, the bleach performance characteristics of such peroxygen bleaches are much less desirable than those of the halogen bleaching agents. Therefore, liquid aqueous activated peroxygen bleach-containing compositions have been developed containing activators, i.e., compounds which enhance peroxygen bleaching performance.

[0004] It is an object of the present invention to provide a bleaching composition which not only delivers effective bleaching performance, when used in laundry applications, but is also safe to the surfaces treated, e.g. to fabrics per se and/or colours of fabrics.

[0005] It is often preferred, from a consumer acceptability standpoint, that detergent compositions be coloured. This is especially true of liquid detergent compositions. However, colouring agents for example pigments and dyes are often not stable or not sufficiently stable to oxidative bleaching agents. Furthermore, colouring agents can also be susceptible to the chemical environment into which they are formulated e.g. pH of the composition. This is also most often true when the composition is in liquid form as the components of the composition are free to migrate throughout the liquid, potentially reacting with each other and consequently resulting in the depletion of some components e.g. bleaching agents and/or colouring agents. It is thus a further objective of the present invention to provide a liquid bleaching composition that additionally comprises a colouring agent and that is chemically stable, and more particularly chemically stable on storage.

[0006] The compositions according to the present invention may be useful in any laundry application, e.g., as a laundry detergent or a laundry additive, and when used as a laundry pretreater. A particular advantage of the compositions of the present invention is that they are suitable for the bleaching of different types of fabrics including natural fabrics, (e.g., fabrics made of cotton, and linen), synthetic fabrics such as those made of polymeric fibers of synthetic origin (e.g., polyamide-elasthane) as well as those made of both natural and synthetic fibers. For example, the bleaching compositions of the present invention herein may be used on synthetic fabrics despite a standing prejudice against using bleaches on synthetic fabrics, as evidenced by warnings on labels of clothes and commercially available bleaching compositions like hypochlorite-containing compositions.

[0007] Another advantage of the bleaching compositions according to the present invention is that they can be used in a variety of conditions, i.e., in hard and soft water as well as when used neat or diluted. More particularly, it has been found that the liquid aqueous compositions of the present invention find a preferred application when used in their diluted form in any application and especially in any conventional laundry application. Indeed, upon dilution (typically at a dilution level of 20ml/L or more (composition:water) the compositions of the present invention become less acidic, e.g., from a pH of about 1.5 to about 6.5 or more. The compositions according to the present invention although delivering effective bleaching performance in their neat form surprisingly exhibit further enhanced bleaching performance in their diluted form. Actually, this "pH jump" effect allows to formulate acidic liquid aqueous compositions (i.e. pH below 7, preferably below 5) which are physically and chemically stable upon prolonged periods of storage and which deliver outstanding bleaching performance under diluted usage conditions.

Summary of the invention

[0008] According to the present invention there is provided a liquid bleaching composition comprising a preformed peroxy carboxylic acid and a metal phthalocyanine colouring agent.

[0009] The present invention further encompasses a process of bleaching a surface and the use of said composition.

Detailed description of the invention

The bleaching composition

[0010] The compositions according to the present invention are liquid compositions as opposed to a solid or a gas. As used herein the term "liquid" includes suspensions of solid particles in liquid compositions and "pasty" compositions. The liquid compositions herein are preferably aqueous compositions, comprising water at a level of preferably 10% to 99%, more preferably from 50% to 98% by weight of the bleaching composition. The liquid compositions according to the present invention have a pH below 7. Preferably, the pH of the compositions according to the present invention is from 0.1 to 6.5, more preferably from 0.5 to 5, even more preferably from 2 to 4. Formulating the compositions according to the present invention in the acidic pH range is critical to the chemical stability of the compositions according to the present invention. The pH of the composition is preferably below the pKa of the peracid used.

[0011] The pH of the compositions may be adjusted by any acid or alkaline species known to those skilled in the art. Examples of acidic species suitable for use herein are organic acids, such as citric acid and inorganic acids, such as sulphuric acid, sulphonic acid and/or metanesulphonic acid. Examples of alkaline species are sodium hydroxide, potassium hydroxide and/or sodium carbonate. Other pH adjusting agents include the alkanolamines. It may be advantageous to use alkanolamines, in particular monoethanolamine, inasmuch as they have an additional effect of regulating the viscosity of the emulsion, without compromising on its physical stability.

[0012] The bleaching performance of the present composition may be evaluated by the following test methods on various type of bleachable stains.

[0013] An advantage of the compositions of the present invention is that they are physically and chemically stable upon prolonged periods of storage.

[0014] Chemical stability of the bleaching agent herein may be evaluated by measuring the concentration of available oxygen at given storage time after having manufactured the compositions. By "chemically stable", it is meant herein that the compositions of the present invention comprising a peracid do not undergo more than 30% AvO loss, in 10 days at 35°C and preferably not more than 20% AvO loss.

[0015] The loss of available oxygen (AvO) of a peracid-containing composition over time can be measured with the iodometric titration method in which the peracid is reduced by excess potassium iodide and the iodine formed is determined by titration with sodium thiosulphate. This method is well known in the art and is reported for example in A Bleachers Handbook by and available from Interox. Alternatively peracid concentration can also be measured using a chromatography method described in the literature for peracids (F. Di Furia et al., Gas-liquid Chromatography Method for Determination of Peracids, Analyst, Vol 113, May 1988, p 793-795).

[0016] Chemical stability of the colouring agent may be evaluated according to a visual scale of colour intensity and loss thereof over time as compared to a freshly prepared reference (as described herein after).

[0017] By "physically stable", it is meant herein that no phase separation occurs in the compositions according to the present invention for a period of 7 days at 35°C meaning that there is no separation of a two liquid phases and equally there is no precipitation or flocculation of a solid phase from a liquid phase i.e. a solid particle remains homogeneously distributed throughout the liquid composition.

Pre-formed Peroxy Carboxylic acid

[0018] The bleaching composition of the present invention comprises a pre-formed peroxy carboxylic acid (hereafter referred to as peracid). Any suitable peracid known in the art may be used herein.
Preferably the peracid is in solid form.

[0019] In a preferred embodiment of the present invention the peracid has the general formula

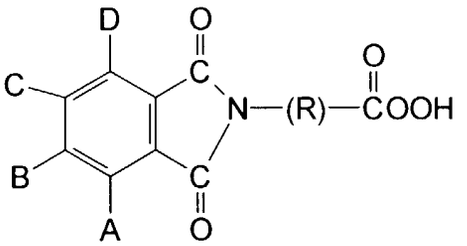
X-R-C(O)OOH

wherein R is a linear or branched alkyl chain having at least 1 carbon atoms and X is hydrogen or a substituent group selected from the group consisting of alkyl, especially alkyl chains of from 1 to 24 carbon atoms, aryl, halogen, ester, ether, amine, amide, substituted phthalic amino, imide, hydroxide, sulphide, sulphate, sulphonate, carboxylic, heterocyclic, nitrate, aldehyde, phosphonate, phosphonic or mixtures thereof.

[0020] More particularly the R group preferably comprises up to 24 carbon atoms. Alternatively, the R group may be a branched alkyl chain comprising one or more side chains which comprise substituent groups selected from the group consisting of aryl, halogen, ester, ether, amine, amide, substituted phthalic amino, imide, hydroxide, sulphide, sulphate,

sulphonate, carboxylic, heterocyclic, nitrate, aldehyde, ketone or mixtures thereof.

[0021] In a preferred peracid the X group, according to the above general formula, is phthalimido group. Thus, particularly preferred peracids are those having general formula:



where R is C1-20 and where A, B, C and D are independently either hydrogen or substituent groups individually selected from the group consisting of alkyl, hydroxyl, nitro, halogen, amine, ammonium, cyanide, carboxylic, sulphate, sulphonate, aldehydes or mixtures thereof.

[0022] In a preferred aspect of the present invention R is an alkyl group having from 3 to 12 carbon atoms, more preferably from 5 to 9 carbon atoms. Preferred substituent groups A, B, C and D are linear or branched alkyl groups having from 1 to 5 carbon atoms, but more preferably hydrogen.

[0023] Preferred peracids are selected from the group consisting of phthaloyl amido peroxy hexanoic acid, phthaloyl amido peroxy heptanoic acid, phthaloyl amido peroxy octanoic acid, phthaloyl amido peroxy nonanoic acid, phthaloyl amido peroxy decanoic acid and mixtures thereof.

[0024] In a particularly preferred aspect of the present invention the peracid has the formula such that R is C_5H_{10} i. e. phthaloyl amido peroxy hexanoic acid or PAP. This peracid is preferably used as a substantially water-insoluble solid or wetcake and is available from Ausimont under the trade name Euroco.

[0025] The peracid is preferably used at a level of from 0.1% to 30%, more preferably from 0.5% to 18% and most preferably 1% to 12% by weight of the composition.

Colouring agent

[0026] The compositions of the present invention require a metal phthalocyanine colouring agent as an essential feature thereof. The Applicants have found that, as discussed above, in order to maintain the stability of the peracid, the composition must be formulated in the acidic pH range. However typically colouring agents are not stable or not sufficiently stable in a peracid-containing environment and additionally are not stable in acidic conditions. The Applicants have identified a group of colouring agents that are stable not only in the presence of peracid, but also in acidic conditions. This group of colouring agents is the metal phthalocyanines.

[0027] The metal ion of the colouring agent is preferably copper, iron, cobalt or nickel.

[0028] Colouring agents are classified according to a recognised international standard known as the Colour Index (most recently published as the 3rd edition from The Society of Dyers and Colourists and the American Association of Textile Chemists and Colourists). Examples of commerically available metal phthalocyanine colouring agents are those available having the colour index number CI 74260 Pigment Green 7 such as those sold under the tradenames Pigmasol Green from BASF, CI 74160 Pigment blue 15 or 15:1 or 15:2 such as Cosmenyl Blue from Clariant, CI 74160 Pigment blue 15:3 such as luconyl blue from BASF and mixtures thereof.

[0029] The colouring agents may be used in solid or liquid form. It is typical however that dyes are generally available in liquid form and pigments are available in solid form. Where a solid form colouring agent is used the size distribution of the particles is preferably less than 200microns, more preferably in the range of from 0.01 to 100 microns and most preferably from 0.1 to 50 microns.

[0030] Typically the colouring agent is present at a level of from 0.00001% to 0.1%, more preferably from 0.0001% to 0.001% and most preferably from 0.002% to 0.005% by weight of the composition.

Optional ingredients

[0031] The compositions herein may further comprise a variety of other optional ingredients such as surfactants, chelating agents, radical scavengers, antioxidants, stabilisers, builders, soil suspending polymer, polymeric soil release agents, pH control agents, dye transfer inhibitor, solvents, suds controlling agents, suds booster, optical brighteners, perfumes and the like.

Surfactants

[0032] The compositions of the present invention may optionally, although preferably comprise a surfactant. The surfactants are selected from the group consisting of nonionic surfactants, anionic surfactants, cationic surfactants, zwitterionic surfactants and/or amphoteric surfactants.

[0033] Suitable anionic surfactants for use 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 ammonium 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 C_{12}-$_{16}$ are preferred for lower wash temperatures (e.g., below about 50°C) and C_{16}-$_{18}$ alkyl chains are preferred for higher wash temperatures (e.g., above about 50°C).

[0034] Other suitable anionic surfactants for use herein are water-soluble salts or acids of the formula $RO(A)_mSO_3M$ 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 about 0.5 and about 6, more preferably between about 0.5 and about 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 C_{12}-C_{18} alkyl polyethoxylate (1.0) sulfate, C_{12}-$C_{18}E(1.0)M$), C_{12}-C_{18} alkyl polyethoxylate (2.25) sulfate, C_{12}-$C_{18}E(2.25)M$), C_{12}-C_{18} alkyl polyethoxylate (3.0) sulfate C_{12}-$C_{18}E(3.0)$, and C_{12}-C_{18} alkyl polyethoxylate (4.0) sulfate C_{12}-$C_{18}E(4.0)M$), wherein M is conveniently selected from sodium and potassium.

[0035] Other particularly suitable anionic surfactants for use herein are alkyl sulphonates including water-soluble salts or acids of the formula RSO_3M wherein R is a C_6-C_{22} linear or branched, saturated or unsaturated alkyl group, preferably a C_{12}-C_{18} alkyl group and more preferably a C_{14}-C_{16} alkyl group, 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 ammonium 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).

[0036] Suitable alkyl aryl sulphonates for use herein include water- soluble salts or acids of the formula RSO_3M wherein R is an aryl, preferably a benzyl, substituted by a C_6-C_{22} linear or branched saturated or unsaturated alkyl group, preferably a C_{12}-C_{18} alkyl group and more preferably a C_{14}-C_{16} alkyl group, and M is H or a cation, e.g., an alkali metal cation (e.g., sodium, potassium, lithium, calcium, magnesium etc) or ammonium or substituted ammonium (e.g., methyl-, dimethyl-, and trimethyl ammonium 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).

[0037] The alkylsulfonates and alkyl aryl sulphonates for use herein include primary and secondary alkylsulfonates and primary and secondary alkyl aryl sulphonates. By "secondary C6-C22 alkyl or C6-C22 alkyl aryl sulphonates", it is meant herein that in the formula as defined above, the SO3M or aryl-SO3M group is linked to a carbon atom of the alkyl chain being placed between two other carbons of the said alkyl chain (secondary carbon atom).

[0038] For example C14-C16 alkyl sulphonate salt is commercially available under the name Hostapur ® SAS from Hoechst and C8-alkylsulphonate sodium salt is commercially available under the name Witconate NAS 8® from Witco SA. An example of commercially available alkyl aryl sulphonate is Lauryl aryl sulphonate from Su.Ma. Particularly preferred alkyl aryl sulphonates are alkyl benzene sulphonates commercially available under trade name Nansa® available from Albright & Wilson.

[0039] 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_8-C_{24} olefinsulfonates, sulfonated polycarboxylic acids prepared by sulfonation of the pyrolyzed product of alkaline earth metal citrates, e.g., as described in British patent specification No. 1,082,179, C_8-C_{24} alkylpolyglycolethersulfates (containing up to 10 moles of ethylene oxide); alkyl ester sulfonates such as C_{14-16} methyl ester sulfonates; acyl glycerol sulfonates, fatty oleyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, paraffin sulfonates, alkyl phosphates, isethionates such as the acyl isethionates, N-acyl taurates, alkyl succinamates and sulfosuccinates, monoesters of sulfosuccinate (especially saturated and unsaturated C_{12}-C_{18} monoesters) diesters of sulfosuccinate (especially saturated and unsaturated C_6-C_{14} 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 $RO(CH_2CH_2O)_kCH_2COO\text{-}M^+$ wherein R is a C_8-C_{22} 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 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).

[0040] Other particularly suitable anionic surfactants for use herein are alkyl carboxylates and alkyl alkoxycarboxylates having from 4 to 24 carbon atoms in the alkyl chain, preferably from 8 to 18 and more preferably from 8 to 16, wherein the alkoxy is propoxy and/or ethoxy and preferably is ethoxy at an alkoxylation degree of from 0.5 to 20, preferably from 5 to 15. Preferred alkylalkoxycarboxylate for use herein is sodium laureth 11 carboxylate (i.e., $RO(C_2H_4O)_{10}\text{-}CH_2COONa$, with R= C12-C14) commercially available under the name Akyposoft® 100NV from Kao Chemical Gbmh.

[0041] Suitable amphoteric surfactants for use herein include amine oxides having the following formula $R_1R_2R_3NO$ wherein each of R1, R2 and R3 is independently a saturated substituted or unsubstituted, linear or branched hydrocarbon chain of from 1 to 30 carbon atoms. Preferred amine oxide surfactants to be used according to the present invention are amine oxides having the following formula $R_1R_2R_3NO$ 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 hydrocarbon chain. Suitable amine oxides for use herein are for instance natural blend C8-C10 amine oxides as well as C12-C16 amine oxides commercially available from Hoechst.

[0042] Suitable zwitterionic 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 sulfonates, although other groups like sulfates, phosphonates, and the like can be used. A generic formula for the zwitterionic surfactants to be used herein is :

$$R_1\text{-}N^+(R_2)(R_3)R_4X^-$$

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 carboxylic acid group or a C_1-C_6 sulfonate 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 sulfonate group.

[0043] 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 amido radical of the formula $R_a\text{-}C(O)\text{-}NH\text{-}(C(R_b)_2)_m$, 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.

[0044] Preferred R_2 is hydrogen, or a C_1-C_3 alkyl and more preferably methyl. Preferred R_3 is a C_1-C_4 carboxylic acid group or C1-C4 sulfonate group, or a C_1-C_3 alkyl and more preferably methyl. Preferred R_4 is $(CH2)_n$ wherein n is an integer from 1 to 10, preferably from 1 to 6, more preferably is from 1 to 3.

[0045] Some common examples of betaine/sulphobetaine are described in U.S. Pat. Nos. 2,082,275, 2,702,279 and 2,255,082, incorporated herein by reference.

[0046] 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 Albright & Wilson under the trade name Empigen BB/L®.

[0047] Examples of amidobetaines include cocoamidoethylbetaine, cocoamidopropyl betaine or C10-C14 fatty acylamidopropylene(hydropropylene)sulfobetaine. For example C10-C14 fatty acylamidopropylene(hydropropylene)sulfobetaine is commercially available from Sherex Company under the trade name "Varion CAS® sulfobetaine".

[0048] A further example of betaine is Lauryl-immino-dipropionate commercially available from Rhone-Poulenc under the trade name Mirataine H2C-HA ®.

[0049] Suitable cationic surfactants for use herein include derivatives of quaternary ammonium, phosphonium, imidazolium and sulfonium compounds. Preferred cationic surfactants for use herein are quaternary ammonium compounds wherein one or two of the hydrocarbon groups linked to nitrogen are a saturated, linear or branched alkyl group of 6 to 30 carbon atoms, preferably of 10 to 25 carbon atoms, and more preferably of 12 to 20 carbon atoms, and wherein the other hydrocarbon groups (i.e. three when one hydrocarbon group is a long chain hydrocarbon group as mentioned hereinbefore or two when two hydrocarbon groups are long chain hydrocarbon groups as mentioned hereinbefore) linked to the nitrogen are independently substituted or unsubstituted, linear or branched, alkyl chain of from 1 to 4 carbon atoms, preferably of from 1 to 3 carbon atoms, and more preferably are methyl groups. Preferred quaternary ammonium compounds suitable for use herein are non-chloride/non halogen quaternary ammonium compounds. The counterion used in said quaternary ammonium compounds are compatible with any peracid and are selected from the group of methyl sulfate, or methylsulfonate, and the like.

[0050] Particularly preferred for use in the compositions of the present invention are trimethyl quaternary ammonium compounds like myristyl trimethylsulfate, cetyl trimethylsulfate and/or tallow trimethylsulfate. Such trimethyl quaternary ammonium compounds are commercially available from Hoechst, or from Albright & Wilson under the trade name EMPIGEN CM®.

[0051] Amongst the nonionic surfactants, alkoxylated nonionic surfactants and especially ethoxylated nonionic surfactants are suitable for use herein.

[0052] Suitable capped alkoxylated nonionic surfactants for use herein are according to the formula:

$$R_1(O\text{-}CH_2\text{-}CH_2)_n\text{-}(OR_2)_m\text{-}O\text{-}R_3$$

wherein R_1 is a C_8-C_{24} linear or branched alkyl or alkenyl group, aryl group, alkaryl group, preferably R_1 is a C_8-C_{18} alkyl or alkenyl group, more preferably a C_{10}-C_{15} alkyl or alkenyl group, even more preferably a C_{10}-C_{15} alkyl group; wherein R_2 is a C_1-C_{10} linear or branched alkyl group, preferably a C_2-C_{10} linear or branched alkyl group; wherein R_3 is a C_1-C_{10} alkyl or alkenyl group, preferably a C_1-C_5 alkyl group, more preferably methyl; and wherein n and m are integers independently ranging in the range of from 1 to 20, preferably from 1 to 10, more preferably from 1 to 5; or mixtures thereof.

[0053] These surfactants are commercially available from BASF under the trade name Plurafac®, from HOECHST under the trade name Genapol® or from ICI under the trade name Symperonic®. Preferred capped nonionic alkoxylated surfactants of the above formula are those commercially available under the tradename Genapol® L 2.5 NR from Hoechst, and Plurafac® from BASF.

[0054] Particularly preferred surfactants are those selected from the group consisting of alkyl sulphate, alkyl sulphonate, alkyl ethoxy sulphate, alkyl benzene sulphonate, alkyl carboxylate, alkyl ethoxy carboxylate, amine oxides and mixtures thereof. More preferably the surfactant system comprises an alkyl sulphonate and an amine oxide.

[0055] Typically, the compositions according to the present invention preferably comprise the surfactant system at a level of from 0.01% to 30%, preferably from 0.1% to 15 % and more preferably less than 10% and most preferably from 0.2% to 5% by weight of the composition.

Suspending agent

[0056] The composition of the present invention may preferably comprise a suspending agent. A suspending agent is an ingredient which is specifically added to the composition of the present invention to suspend a solid particulate ingredient of the composition. With regard to the present invention, a suspending agent is particularly useful for suspending the peracid, where the peracid is present as a solid, and the colouring agent, where insoluble or substantially insoluble.

[0057] Suitable suspending agents are those known in the art. Examples of suspending agents include gum-type polymers (e.g. xanthan gum), polyvinyl alcohol and derivatives thereof, cellulose and derivatives thereof and polycarboxylate polymers.

[0058] In a particularly preferred embodiment of the present invention the suspending agent comprises a gum-type polymer or a polycarboxylate polymer. Particularly preferred examples of these suspending agents are xanthan gum and cross-linked polycarboxylate polymer respectively.

[0059] The gum-type polymer may be selected from the group consisting of polysaccharide hydrocolloids, xanthan gum, guar gum, succinoglucan gum, Cellulose, derivatives of any of the above and mixtures thereof. In a preferred aspect of the present invention the gum-type polymer is a xanthan gum or derivative thereof.

[0060] The gum-type polymer is preferably present at a level of from 0.01% to 10%, most preferably from 0.1% to 3%.

[0061] The polycarobxylate polymer can be a homo or copolymer of monomer units selected from acrylic acid, methacrylic acid, maleic acid, malic acid, maleic anhydride. Preferred polycarboxylate polymers are Carbopol from BF

Goodrich. Suitable polymers have molecular weight in the range of from 10000 to 100 000 000 most preferably 1 000 000 to 10 000 000.

[0062] The cross-linked polycarboxylate polymer is preferably present at a level of from 0.01% to 2% more preferably from 0.01% to 1%, most preferably from 0.1%to 0.8%.

[0063] In an alternative embodiment the suspending agent comprises a combination of at least two polymers. In this embodiment the first polymer is a gum-type polymer and the second is a cross-linked polycarboxylate polymer. The composition may additionally comprise further polymers.

[0064] The ratio of gum-type polymer to cross-linked polycarboxylate polymer is from 100:1 to 1:100, most preferably from 1:10 to 10:1.

Chelating agents

[0065] The compositions of the present invention 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.

[0066] The presence of chelating agents contribute to further enhance the chemical stability of the compositions. A chelating agent may be also desired in the compositions of the present invention as it allows to increase the ionic strength of the compositions herein and thus their stain removal and bleaching performance on various surfaces.

[0067] Suitable phosphonate chelating agents for use herein may include alkali metal ethane 1-hydroxy diphosphonates (HEDP), alkylene poly (alkylene phosphonate), as well as amino phosphonate compounds, including amino 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 Monsanto under the trade name DEQUEST®.

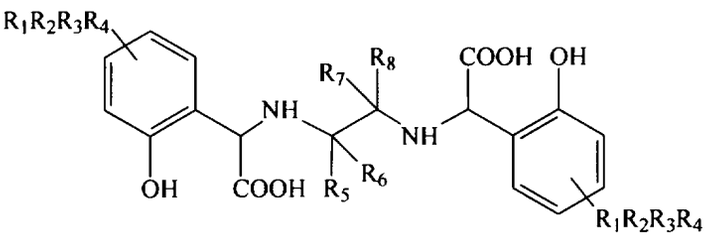
[0068] Polyfunctionally-substituted aromatic chelating agents may also be useful in the compositions herein. See U. S. patent 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy -3,5-disulfobenzene.

[0069] 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 acids is, for instance, commercially available under the tradename ssEDDS® from Palmer Research Laboratories.

[0070] 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).

[0071] Further carboxylate chelating agents to be used herein include salicylic acid, aspartic acid, glutamic acid, glycine, malonic acid or mixtures thereof.

[0072] Another chelating agent for use herein is of the formula:



wherein R_1, R_2, R_3, and R_4 are independently selected from the group consisting of -H, alkyl, alkoxy, aryl, aryloxy, -Cl,

-Br, -NO_2, -C(O)R', and-SO_2R"; 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 R_5, R_6, R_7, and R_8 are independently selected from the group consisting of -H and alkyl.

[0073] 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.

[0074] Typically, the compositions according to the present invention comprise up to 5% by weight of the total composition of a chelating agent, or mixtures thereof, preferably from 0.01% to 1.5% by weight and more preferably from 0.01% to 0.5%.

Radical scavengers

[0075] The compositions of the present invention may comprise a radical scavenger or a mixture thereof.

[0076] 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 be commercially available from Nipa Laboratories under the trade name Nipanox S1 ®.

[0077] Radical scavengers when used, are typically present herein in amounts up to 10% by weight of the total composition and preferably from 0.001% to 0.5% by weight.

[0078] The presence of radical scavengers may contribute to the chemical stability of the bleaching compositions of the present invention as well as to the safety profile of the compositions of the present invention.

Suds controlling agents

[0079] The compositions according to the present invention may further comprise a suds controlling agent such as 2-alkyl alkanol, or mixtures thereof, as a preferred optional ingredient. Particularly suitable to be used in the present invention are the 2-alkyl alkanols having an alkyl chain comprising from 6 to 16 carbon atoms, preferably from 8 to 12 and a terminal hydroxy group, said alkyl chain being substituted in the α position by an alkyl chain comprising from 1 to 10 carbon atoms, preferably from 2 to 8 and more preferably 3 to 6. Such suitable compounds are commercially available, for instance, in the Isofol® series such as Isofol® 12 (2-butyl octanol) or Isofol® 16 (2-hexyl decanol).

[0080] Other suds controlling agents may include alkali metal (e.g., sodium or potassium) fatty acids, or soaps thereof, containing from about 8 to about 24, preferably from about 10 to about 20 carbon atoms.

[0081] The fatty acids including those used in making the soaps can be obtained from natural sources such as, for instance, plant or animal-derived glycerides (e.g., palm oil, coconut oil, babassu oil, soybean oil, castor oil, tallow, whale oil, fish oil, tallow, grease, lard and mixtures thereof). The fatty acids can also be synthetically prepared (e.g., by oxidation of petroleum stocks or by the Fischer-Tropsch process).

[0082] Alkali metal soaps can be made by direct saponification of fats and oils or by the neutralization of the free fatty acids which are prepared in a separate manufacturing process. Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from coconut oil and tallow, i.e., sodium and potassium tallow and coconut soaps.

[0083] The term "tallow" is used herein in connection with fatty acid mixtures which typically have an approximate carbon chain length distribution of 2.5% C14, 29% C16, 23% C18, 2% palmitoleic, 41.5% oleic and 3% linoleic (the first three fatty acids listed are saturated). Other mixtures with similar distribution, such as the fatty acids derived from various animal tallows and lard, are also included within the term tallow. The tallow can also be hardened (i.e., hydrogenated) to convert part or all of the unsaturated fatty acid moieties to saturated fatty acid moieties.

[0084] When the term "coconut" is used herein it refers to fatty acid mixtures which typically have an approximate carbon chain length distribution of about 8% C8, 7% C10, 48% C12, 17% C14, 9% C16, 2% C18, 7% oleic, and 2% linoleic (the first six fatty acids listed being saturated). Other sources having similar carbon chain length distribution such as palm kernel oil and babassu oil are included with the term coconut oil.

[0085] Other suitable suds controlling agents are exemplified by silicones, and silica-silicone mixtures. Silicones can be generally represented by alkylated polysiloxane materials while silica is normally used in finely divided forms exemplified by silica aerogels and xerogels and hydrophobic silicas of various types. These materials can be incorporated as particulates in which the suds controlling agent is advantageously releasable incorporated in a water-soluble or water-dispersible, substantially non-surface-active detergent impermeable carrier. Alternatively the suds controlling agent can be dissolved or dispersed in a liquid carrier and applied by spraying on to one or more of the other compo-

nents.

[0086] A preferred silicone suds controlling agent is disclosed in Bartollota et al. U.S. Patent 3 933 672. Other particularly useful suds controlling agents are the self-emulsifying silicone suds controlling agents, described in German Patent Application DTOS 2 646 126 published April 28, 1977. An example of such a compound is DC-544, commercially available from Dow Corning, which is a siloxane-glycol copolymer.

[0087] Especially preferred silicone suds controlling agents are described in Copending European Patent application N°92201649.8. Said compositions can comprise a silicone/silica mixture in combination with fumed nonporous silica such as Aerosil^{R}.

[0088] A preferred type of suds controlling agent is an alkyl capped alcohol alkoxylate. The alkyl chain of the alcohol can be from C3-C30, the alkoxylate is preferably ethoxylate comprising preferably from 1 to 30 moles thereof and the cap is preferably a C1-C6 linear or branched alkyl group.

[0089] Especially preferred suds controlling agent are the suds controlling agent system comprising a mixture of silicone oils and the 2-alkyl-alcanols.

[0090] Typically, the compositions herein may comprise up to 4% by weight of the total composition of a suds controlling agent, or mixtures thereof, preferably from 0.1% to 1.5% and most preferably from 0.1% to 0.8%.

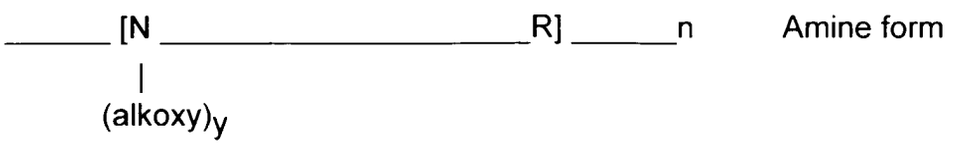
Stabilisers

[0091] The compositions of the present invention may further comprise up to 10%, preferably from 2% to 4% by weight of the total composition of an alcohol according to the formula HO - CR'R" - OH, wherein R' and R" are independently H or a C2-C10 hydrocarbon chain and/or cycle. Preferred alcohol according to that formula is propanediol. Indeed, we have observed that these alcohols in general and propanediol in particular also improve the chemical stability of the compositions.

[0092] Other stabilizers like inorganic stabilizers may be used herein. Examples of inorganic stabilizers include sodium stannate and various alkali metal phosphates such as the well-known sodium tripolyphosphates, sodium pyrophosphate and sodium orthophosphate.

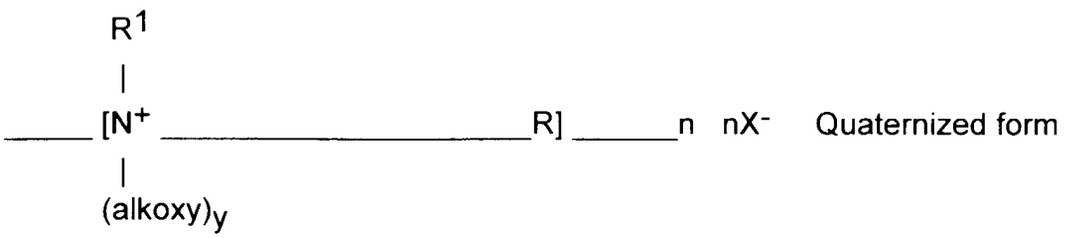
Soil suspending polymer

[0093] The compositions according to the present invention may further comprise a soil suspending polymer, for example a polyamine soil suspending polymer or mixtures thereof, as optional ingredient. Any soil suspending polyamine polymer known to those skilled in the art may be used herein. Particularly suitable polyamine polymers for use herein are polyalkoxylated polyamines. Such materials can conveniently be represented as molecules of the empirical structures with repeating units :



Amine form

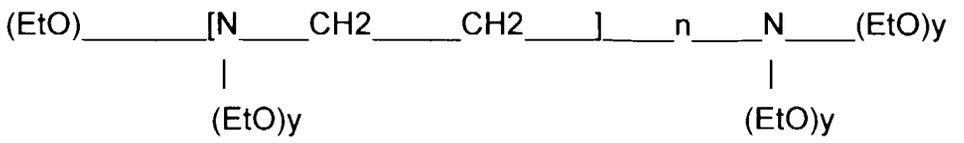
and



Quaternized form

wherein R is a hydrocarbyl group, usually of 2-6 carbon atoms; R^1 may be a C_1-C_{20} hydrocarbon; the alkoxy groups are ethoxy, propoxy, and the like, and y is 2-30, most preferably from 10-20; n is an integer of at least 2, preferably from 2-20, most preferably 3-5; and X^- is an anion such as halide or methylsulfate, resulting from the quaternization reaction.

[0094] The most highly preferred polyamines for use herein are the so-called ethoxylated polyethylene amines, i.e., the polymerized reaction product of ethylene oxide with ethyleneimine, having the general formula :



when y = 2-30. Particularly preferred for use herein is an ethoxylated polyethylene amine, in particular ethoxylated tetraethylenepentamine, and quaternized ethoxylated hexamethylene diamine.

[0095] Soil suspending polyamine polymers contribute to the benefits of the present invention, i.e., that when added on top of said diacyl peroxide, further improve the stain removal performance of a composition comprising them, especially under laundry pretreatment conditions, as described herein. Indeed, they allow to improve the stain removal performance on a variety of stains including greasy stains, enzymatic stains, clay/mud stains as well as on bleachable stains.

[0096] Typically, the compositions comprise up to 10% by weight of the total composition of such a soil suspending polyamine polymer or mixtures thereof, preferably from 0.1% to 5% and more preferably from 0.3% to 2%.

[0097] The compositions herein may also comprise other polymeric soil release agents known to those skilled in the art. Such polymeric soil release agents are characterised by having both hydrophilic segments, to hydrophilize the surface of hydrophobic fibres, such as polyester and nylon, and hydrophobic segments, to deposit upon hydrophobic fibres and remain adhered thereto through completion of washing and rinsing cycles and, thus, serve as an anchor for the hydrophilic segments. This can enable stains occurring subsequent to treatment with the soil release agent to be more easily cleaned in later washing procedures.

[0098] The polymeric soil release agents useful herein especially include those soil release agents having: (a) one or more nonionic hydrophile components consisting essentially of (i) polyoxyethylene segments with a degree of polymerization of at least 2, or (ii) oxypropylene or polyoxypropylene segments with a degree of polymerization of from 2 to 10, wherein said hydrophile segment does not encompass any oxypropylene unit unless it is bonded to adjacent moieties at each end by ether linkages, or (iii) a mixture of oxyalkylene units comprising oxyethylene and from 1 to about 30 oxypropylene units wherein said mixture contains a sufficient amount of oxyethylene units such that the hydrophile component has hydrophilicity great enough to increase the hydrophilicity of conventional polyester synthetic fiber surfaces upon deposit of the soil release agent on such surface, said hydrophile segments preferably comprising at least about 25% oxyethylene units and more preferably, especially for such components having about 20 to 30 oxypropylene units, at least about 50% oxyethylene units; or (b) one or more hydrophobe components comprising (i) C_3 oxyalkylene terephthalate segments, wherein, if said hydrophobe components also comprise oxyethylene terephthalate, the ratio of oxyethylene terephthalate:C_3 oxyalkylene terephthalate units is about 2:1 or lower, (ii) C_4-C_6 alkylene or oxy C_4-C_6 alkylene segments, or mixtures therein, (iii) poly (vinyl ester) segments, preferably polyvinyl acetate), having a degree of polymerization of at least 2, or (iv) C_1-C_4 alkyl ether or C_4 hydroxyalkyl ether substituents, or mixtures therein, wherein said substituents are present in the form of C_1-C_4 alkyl ether or C_4 hydroxyalkyl ether cellulose derivatives, or mixtures therein, and such cellulose derivatives are amphiphilic, whereby they have a sufficient level of C_1-C_4 alkyl ether and/or C_4 hydroxyalkyl ether units to deposit upon conventional polyester synthetic fiber surfaces and retain a sufficient level of hydroxyls, once adhered to such conventional synthetic fiber surface, to increase fiber surface hydrophilicity, or a combination of (a) and (b).

[0099] Typically, the polyoxyethylene segments of (a)(i) will have a degree of polymerization of from about 1 to about 200, although higher levels can be used, preferably from 3 to about 150, more preferably from 6 to about 100. Suitable oxy C_4-C_6 alkylene hydrophobe segments include, but are not limited to, end-caps of polymeric soil release agents such as $MO_3S(CH_2)_nOCH_2CH_2O$-, where M is sodium and n is an integer from 4-6, as disclosed in U.S. Patent 4,721,580, issued January 26, 1988 to Gosselink.

[0100] Polymeric soil release agents useful in the present invention also include cellulosic derivatives such as hydroxyether cellulosic polymers, co-polymeric blocks of ethylene terephthalate or propylene terephthalate with polyethylene oxide or polypropylene oxide terephthalate, and the like. Such agents are commercially available and include hydroxyethers of cellulose such as METHOCEL (Dow). Cellulosic soil release agents for use herein also include those selected from the group consisting of C_1-C_4 alkyl and C_4 hydroxyalkyl cellulose; see U.S. Patent 4,000,093, issued December 28, 1976 to Nicol, et al.

[0101] Soil release agents characterised by poly(vinyl ester) hydrophobe segments include graft co-polymers of poly

(vinyl ester), e.g., C_1-C_6 vinyl esters, preferably poly(vinyl acetate) grafted onto polyalkylene oxide backbones, such as polyethylene oxide backbones. See European Patent Application 0 219 048, published April 22, 1987 by Kud, et al. Commercially available soil release agents of this kind include the SOKALAN type of material, e.g., SOKALAN HP-22, available from BASF (West Germany).

[0102] One type of preferred soil release agent is a co-polymer having random blocks of ethylene terephthalate and polyethylene oxide (PEO) terephthalate. The molecular weight of this polymeric soil release agent is in the range of from about 25,000 to about 55,000. See U.S. Patent 3,959,230 to Hays, issued May 25, 1976 and U.S. Patent 3,893,929 to Basadur issued July 8, 1975.

[0103] Another preferred polymeric soil release agent is a polyester with repeat units of ethylene terephthalate units which contains 10-15% by weight of ethylene terephthalate units together with 90-80% by weight of polyoxyethylene terephthalate units, derived from a polyoxyethylene glycol of average molecular weight 300-5,000. Examples of this polymer include the commercially available material ZELCON 5126 (from Dupont) and MILEASE T (from ICI). See also U.S. Patent 4,702,857, issued October 27, 1987 to Gosselink.

[0104] Another preferred polymeric soil release agent is a sulfonated product of a substantially linear ester oligomer comprised of an oligomeric ester backbone of terephthaloyl and oxyalkyleneoxy repeat units and terminal moieties covalently attached to the backbone. These soil release agents are fully described in U.S. Patent 4,968,451, issued November 6, 1990 to J.J. Scheibel and E.P. Gosselink. Other suitable polymeric soil release agents include the terephthalate polyesters of U.S. Patent 4,711,730, issued December 8, 1987 to Gosselink et al, the anionic end-capped oligomeric esters of U.S. Patent 4,721,580, issued January 26, 1988 to Gosselink, and the block polyester oligomeric compounds of U.S. Patent 4,702,857, issued October 27, 1987 to Gosselink.

[0105] Preferred polymeric soil release agents also include the soil release agents of U.S. Patent 4,877,896, issued October 31, 1989 to Maldonado et al, which discloses anionic, especially sulfoaroyl, end-capped terephthalate esters.

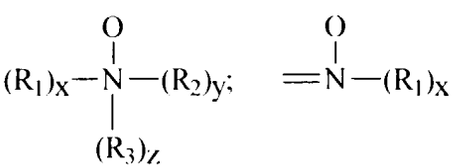
[0106] Still another preferred soil release agent is an oligomer with repeat units of terephthaloyl units, sulfoisoterephthaloyl units, oxyethyleneoxy and oxy-1,2-propylene units. The repeat units form the backbone of the oligomer and are preferably terminated with modified isethionate end-caps. A particularly preferred soil release agent of this type comprises about one sulfoisophthaloyl unit, 5 terephthaloyl units, oxyethyleneoxy and oxy-1,2-propyleneoxy units in a ratio of from about 1.7 to about 1.8, and two end-cap units of sodium 2-(2-hydroxyethoxy)-ethanesulfonate. Said soil release agent also comprises from about 0.5% to about 20%, by weight of the oligomer, of a crystalline-reducing stabilizer, preferably selected from the group consisting of xylene sulfonate, cumene sulfonate, toluene sulfonate, and mixtures thereof. See U.S. Pat. No. 5,415,807, issued May 16, 1995, to Gosselink et al.

[0107] If utilised, soil release agents will generally comprise from 0.01% to 10.0%, by weight, of the detergent compositions herein, typically from 0.1% to 5%, preferably from 0.2% to 3.0%.

Dye transfer inhibitor

[0108] The compositions of the present invention may also include one or more materials effective for inhibiting the transfer of dyes from one dyed surface to another during the cleaning process. Generally, such dye transfer inhibiting agents include polyvinyl pyrrolidone polymers, polyamine N-oxide polymers, co-polymers of N-vinylpyrrolidone and N-vinylimidazole, manganese phthalocyanine, peroxidases, and mixtures thereof. If used, these agents typically comprise from 0.01% to 10% by weight of the composition, preferably from 0.01% to 5%, and more preferably from 0.05% to 2%.

[0109] More specifically, the polyamine N-oxide polymers preferred for use herein contain units having the following structural formula: R-A_x-P; wherein P is a polymerizable unit to which an N-O group can be attached or the N-O group can form part of the polymerizable unit or the N-O group can be attached to both units; A is one of the following structures: -NC(O)-, -C(O)O-, -S-, -O-, -N=; x is 0 or 1; and R is aliphatic, ethoxylated aliphatics, aromatics, heterocyclic or alicyclic groups or any combination thereof to which the nitrogen of the N-O group can be attached or the N-O group is part of these groups. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyridine, pyrrole, imidazole, pyrrolidine, piperidine and derivatives thereof. The N-O group can be represented by the following general structures:



wherein R_1, R_2, R_3 are aliphatic, aromatic, heterocyclic or alicyclic groups or combinations thereof; x, y and z are 0 or 1; and the nitrogen of the N-O group can be attached or form part of any of the aforementioned groups. The amine oxide unit of the polyamine N-oxides has a pKa <10, preferably pKa <7, more preferred pKa <6.

[0110] Any polymer backbone can be used as long as the amine oxide polymer formed is water-soluble and has dye transfer inhibiting properties. Examples of suitable polymeric backbones are polyvinyls, polyalkylenes, polyesters, polyethers, polyamide, polyimides, polyacrylates and mixtures thereof. These polymers include random or block co-polymers where one monomer type is an amine N-oxide and the other monomer type is an N-oxide. The amine N-oxide polymers typically have a ratio of amine to the amine N-oxide of 10:1 to 1:1,000,000. However, the number of amine oxide groups present in the polyamine oxide polymer can be varied by appropriate co-polymerization or by an appropriate degree of N-oxidation. The polyamine oxides can be obtained in almost any degree of polymerization. Typically, the average molecular weight is within the range of 500 to 1,000,000; more preferred 1,000 to 500,000; most preferred 5,000 to 100,000. This preferred class of materials can be referred to as "PVNO". The most preferred polyamine N-oxide useful in the detergent compositions herein is poly(4-vinylpyridine-N-oxide) which as an average molecular weight of about 50,000 and an amine to amine N-oxide ratio of about 1:4.

[0111] Co-polymers of N-vinylpyrrolidone and N-vinylimidazole polymers (referred to as a class as "PVPVI") are also preferred for use herein. Preferably the PVPVI has an average molecular weight range from 5,000 to 1,000,000, more preferably from 5,000 to 200,000, and most preferably from 10,000 to 20,000. (The average molecular weight range is determined by light scattering as described in Barth, et al., Chemical Analysis, Vol 113. "Modern Methods of Polymer Characterization", the disclosures of which are incorporated herein by reference.) The PVPVI co-polymers typically have a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1:1 to 0.2:1, more preferably from 0.8:1 to 0.3:1, most preferably from 0.6:1 to 0.4:1. These co-polymers can be either linear or branched.

[0112] The present invention compositions may also employ a polyvinylpyrrolidone ("PVP") having an average molecular weight of from 5,000 to 400,000, preferably from 5,000 to 200,000, and more preferably from 5,000 to 50,000. PVP's are known to persons skilled in the detergent field; see, for example, EP-A-262,897 and EP-A-256,696, incorporated herein by reference. Compositions containing PVP can also contain polyethylene glycol ("PEG") having an average molecular weight from 500 to 100,000, preferably from 1,000 to 10,000. Preferably, the ratio of PEG to PVP on a ppm basis delivered in wash solutions is from 2:1 to 50:1, and more preferably from 3:1 to 10:1.

Brightener

[0113] Any optical brighteners, fluorescent whitening agents or other brightening or whitening agents known in the art can be incorporated in the instant compositions when they are designed for fabric treatment or laundering, at levels typically from about 0.05% to about 1.2%, by weight, of the detergent compositions herein. Commercial optical brighteners which may be useful in the present invention can be classified into subgroups, which include, but are not necessarily limited to, derivatives of stilbene, pyrazoline, coumarin, carboxylic acids, methinecyanines, dibenzothiophene-5,5-dioxide, azoles, 5and 6-membered-ring heterocyclic brighteners, this list being illustrative and non-limiting. Examples of such brighteners are disclosed in "The Production and Application of Fluorescent Brightening Agents", M. Zahradnik, Published by John Wiley & Sons, New York (1982).

[0114] Specific examples of optical brighteners which are useful in the present compositions are those identified in U.S. Patent 4,790,856, issued to Wixon on December 13, 1988. These brighteners include the PHORWHITE series of brighteners from Verona. Other brighteners disclosed in this reference include: Tinopal UNPA, Tinopal CBS and Tinopal 5BM, Tinopal PLC, Tinopal SOP, Tinopal SWN, Tinopal K, Uvitex AT all available from Ciba-Geigy; Artic White CC and Artic White CWD, available from Hilton-Davis, located in Italy; the 2-(4-styryl-phenyl)-2H-naphthol[1,2-d]triazoles; 4,4'-bis- (1,2,3-triazol-2-yl)-stilbenes; 4,4'-bis(styryl)bisphenyls; and the aminocoumarins. Specific examples of these brighteners include 4-methyl-7-diethyl- amino coumarin; 1,2-bis(-benzimidazol-2-yl)ethylene; 2,5-bis(benzoxazol-2-yl)thiophene; 2-styryl-napth-[1,2-d]oxazole; and 2-(stilbene-4-yl)-2H-naphtho- [1,2-d]triazole. See also U.S. Patent 3,646,015, issued February 29, 1972, to Hamilton. Anionic brighteners are typically preferred herein.

Suds booster

[0115] If high sudsing is desired, suds boosters such as C_{10}-C_{16} alkanolamides can be incorporated into the compositions, typically at 1%-10% levels. The C_{10}-C_{14} monoethanol and diethanol amides illustrate a typical class of such suds boosters. Use of such suds boosters with high sudsing adjunct surfactants such as the amine oxides, betaines and sultaines noted above is also advantageous. If desired, soluble magnesium salts such as $MgCl_2$, $MgSO_4$, and the like, can be added at levels of, for example, 0.1%-2%, to provide additional suds and to enhance grease removal performance.

Processes of treating surfaces

[0116] In the present invention, the surface to be cleaned is treated with a liquid composition of the present invention.

[0117] By "surfaces", it is meant herein any inanimate surface. These inanimate surfaces include, but are not limited to, hard-surfaces typically found in houses like kitchens, bathrooms, or in car interiors, e.g., tiles, walls, floors, chrome, glass, smooth vinyl, any plastic, plastified wood, table top, sinks, cooker tops, dishes, sanitary fittings such as sinks, showers, shower curtains, wash basins, WCs and the like, as well as fabrics including clothes, curtains, drapes, bed linens, bath linens, table cloths, sleeping bags, tents, upholstered furniture and the like, and carpets. Inanimate surfaces also include household appliances including, but not limited to, refrigerators, freezers, washing machines, automatic dryers, ovens, microwave ovens, dishwashers and so on.

[0118] By "treating a surface", it is meant herein bleaching said surfaces as the compositions of the present invention comprise a bleaching system based on a peracid compound or a mixture thereof and optionally cleaning as said compositions may comprise a surfactant or any other conventional cleaning agents.

[0119] Thus, the present invention also encompasses a process of treating, especially bleaching a fabric, as the inanimate surface. In such a process a composition according to the present invention is contacted with the fabrics to be treated.

[0120] This can be done either in a so-called "pretreatment mode", where a liquid bleaching composition, as defined herein, is applied neat onto said fabrics before the fabrics are rinsed, or washed then rinsed, or in a "soaking mode" where a liquid bleaching composition, as defined herein, is first diluted in an aqueous bath and the fabrics are immersed and soaked in the bath, before they are rinsed, or in a "through the wash mode", where a liquid bleaching composition, as defined herein, is added on top of a wash liquor formed by dissolution or dispersion of a typical laundry detergent. It is also essential in both cases, that the fabrics be rinsed after they have been contacted with said composition, before said composition has completely dried off.

[0121] The compositions according to the present invention may be used in neat or diluted form. However the compositions herein are typically used in diluted form in a laundry operation. By "in diluted form", it is meant herein that the compositions for the bleaching of fabrics according to the present invention may be diluted by the user, preferably with water. Such dilution may occur for instance in hand laundry applications as well as by other means such as in a washing machine. Said compositions can be diluted up to 500 times, preferably from 5 to 200 times and more preferably from 10 to 80 times.

[0122] More specifically, the process of bleaching fabrics according to the present invention comprises the steps of first contacting said fabrics with a bleaching composition according to the present invention, in its diluted form, then allowing said fabrics to remain in contact with said composition, for a period of time sufficient to bleach said fabrics, typically 1 to 60 minutes, preferably 5 to 30 minutes, then rinsing said fabrics with water. If said fabrics are to be washed, i.e., with a conventional detergent composition preferably comprising at least one surface active agent, said washing may be conducted together with the bleaching of said fabrics by contacting said fabrics at the same time with a bleaching composition according to the present invention and said detergent composition, or said washing may be conducted before or after said fabrics have been bleached. Accordingly, said process according to the present invention allows bleaching of fabrics and optionally washing of fabrics with a detergent composition preferably comprising at least one surface active agent before the step of contacting said fabrics with said bleaching composition and/or in the step where said fabrics are contacted with said bleaching composition and/or after the step where said fabrics are contacted with said bleaching composition and before the rinsing step and/or after the rinsing step.

[0123] In another embodiment of the present invention the process of bleaching fabrics comprises the step of contacting fabrics with a liquid bleaching composition according to the present invention, in its neat form and allowing said fabrics to remain in contact with said bleaching composition for a period of time sufficient to bleach said fabrics, typically 5 seconds to 30 minutes, preferably 1 minute to 10 minutes and then rinsing said fabrics with water. If said fabrics are to be washed, i.e., with a conventional composition comprising at least one surface active agent, said washing may be conducted before or after that said fabrics have been bleached. Advantageously, the present invention provides liquid bleaching compositions that may be applied neat onto a fabric to bleach, despite a standing prejudice against using bleach-containing compositions neat on fabrics since the present compositions are safe to colors and fabrics perse.

[0124] Alternatively instead of following the neat bleaching method as described herein above (pretreater application) by a rinsing step with water and/or a conventional washing step with a liquid or powder conventional detergent, the bleaching pre-treatment operation may also be followed by the diluted bleaching process as described herein before either in bucket (hand operation) or in a washing machine.

[0125] It is preferred to perform the bleaching processes herein after said fabrics have been washed with a conventional laundry detergent composition. Indeed, it has been observed that bleaching said fabrics with the compositions according to the present invention (typically diluted bleaching methods) after to washing them with a detergent composition provides superior whiteness and stain removal with less energy and detergent than if said fabrics are bleached

first then washed.

[0126] In another embodiment the present invention also encompasses a process of treating a hard-surface, as the inanimate surface. In such a process a composition, as defined herein, is contacted with the hard-surfaces to be treated. Thus, the present invention also encompasses a process of treating a hard-surface with a composition, as defined herein, wherein said process comprises the step of applying said composition to said hard-surface, preferably only soiled portions thereof, and optionally rinsing said hard-surface.

[0127] In the process of treating hard-surfaces according to the present invention the composition, as defined herein, may be applied to the surface to be treated in its neat form or in its diluted form typically up to 200 times their weight of water, preferably into 80 to 2 times their weight of water, and more preferably 60 to 2 times.

[0128] When used as hard surfaces bleaching/disinfecting compositions the compositions of the present invention are easy to rinse and provide good shine characteristics on the treated surfaces.

[0129] By "hard-surfaces", it is understood any hard-surfaces as mentioned herein before as well as dishes.

Packaging form of the liquid compositions:

[0130] Depending on the end-use envisioned, the compositions herein can be packaged in a variety of containers including conventional bottles, bottles equipped with roll-on, sponge, brusher or sprayers.

[0131] In one embodiment of the present invention the composition is packaged in a two compartment container, wherein the bleaching composition as described herein is packaged in one compartment and a second composition is packaged in the second compartment. In a particularly preferred aspect, the second composition is a conventional heady duty liquid detergent composition, preferably comprising ingredients, particularly bleach-sensitive ingredients such as surfactants, enzymes and perfumes.

Examples

[0132] The invention is further illustrated by the following which are not meant to be limiting. All levels are described in weight percent of the total composition.

	I	II	III	IV	V	VI
PAP	5	5	5	10	10	10
Carbopol ETD 2691	0.3	0.3	0.3	0.3	0.3	0.3
Xanthan gum	0.2	0.2	0.2	0.2	0.2	0.2
Alkyl 3 ethoxy sulphate	4 4 4 4 4 4					
HEDP	0.1	0.1	0.1	0.1	0.1	0.1
Tinopal SOP	0.02	0.02	0.02	0.02	0.02	0.02
Norasol LMW 45N	3 3 3 3 3 3					
perfume						
Colouring agent 1	0.001			0.001		
Colouring agent 2		0.002			0.001	
Colouring agent 3			0.001			0.001
water to balance						
pH	3.8	3.8	3.8	3.8	3.8	3.8

Colouring agent 1 is Pigmosol Green 7
Colouring agent 2 is Cosmenyl Blue A2R
Colouring agent 3 is Luconyl Blue 7080
PAP is pthaloylamido peroxy hexanoic acid
Carbopol ETD 2691 is a polyacylate polymer available from BF Goodrich
Tinopal SOP is a bightener

Norasol LMW 45N is a polyacrylate polymer

Example 2

[0133] The colour storage stability of compositions I, II and III of Example 1 was evaluated against comparison compositions. The comparison compositions comprised identical components at identical level to compositions I, II and III but with different colouring agent that were not metal phthalocyanines i.e Ultramarine Blue and Violet 16. Comparison composition A comprises Ultramarine Blue and comparison composition B comprises Violet 16.

[0134] The colour intensity was visually graded versus a freshly made sample not containing peracid after 7 days at 23°C and 7 days at 35 °C. The results of the colour stability tests show that only the metal phthalocyanine colouring agents are in fact stable to peracid.

[0135] The scale was from 0 to 4 wherein;

0 means I see no perceivable change in colour intensity;
1 means I think there is a small change in colour intensity;
2 means I can see a small change in colour intensity;
3 means I can see a large change in colour intensity;
4 means I can see a very large change in colour intensity.

Composition	I	II	III	A	B
7 days at 23 °C	1	0	0	4	4
7 days at 35 °C	1	1	0	4	4

Example 3

[0136] Example 2 was repeated, but comparing compositions IV, V and VI against comparison compositions C and D. Comparison composition C comprises Ultramarine Blue and comparison composition D comprises Violet 16.

Composition	IV	V	VI	C	D
7 days at 23 °C	2	2	2	4	4
7 days at 35 °C	2	3.5	3	4	4

Claims

1. A liquid bleaching composition comprising a preformed peroxy carboxylic acid and a metal phthalocyanine colouring agent.

2. A bleaching composition according to the preceding claim wherein the composition has a pH of less than 7.

3. A bleaching composition according to any preceding claim wherein the preformed peroxy carboxylic acid has general formula:

X-R-C(O)OOH

wherein R is a linear or branched alkyl chain having at least 1 carbon atoms and X is hydrogen or a substituent group selected from the group consisting of alkyl, especially alkyl chains of from 1 to 24 carbon atoms, aryl, halogen, ester, ether, amine, amide, substituted phthalic amino, imide, hydroxide, sulphide, sulphate, sulphonate, carboxylic, heterocyclic, nitrate, aldehyde, phosphonate, phosphonic or mixtures thereof.

4. A bleaching composition according to any preceding claims wherein the R group of the preformed peroxy carboxylic

acid is a linear alkyl chain comprising up to 24 carbon atoms.

5. A bleaching composition according to any preceding claim wherein the R group of the preformed peroxy carboxylic acid is a branched alkyl chain comprising one or more side chains which comprise substituent groups selected from the group consisting of aryl, halogen, ester, ether, amine, amide, substituted phthalic amino, imide, hydroxide, sulphide, sulphate, sulphonate, carboxylic, heterocyclic, nitrate, aldehyde, ketone or mixtures thereof.

6. A bleaching composition according to any preceding claim wherein the X group of the preformed peroxy carboxylic acid is a phthalimido group.

7. A bleaching composition according to any preceding claim wherein the preformed peroxy carboxylic acid is phthlyol amido peroxyhexanoic acid.

8. A bleaching composition according to any preceding claim wherein the preformed peroxy carboxylic acid is present at a level of from 5% to 12% by weight of the composition.

9. A bleaching composition according to any preceding claim wherein the preformed peroxy carboxylic acid is in solid form.

10. A bleaching composition according to any preceding claim wherein the metal phthalocyanine is selected from copper, iron, cobalt and nickel phthalocyanine.

11. A bleaching composition according to any preceding claim wherein the metal phthalocyanine is selected from the group consisting of compounds having colour index number CI 74260 Pigment Green 7, CI 74160 Pigment blue 15 or 15:1 or 15:2 or 15:3 and mixtures thereof.

12. A bleaching composition according to any preceding claim wherein the metal phthalocyanine is a substantially insoluble solid particle.

13. A process of cleaning a fabric by applying to the fabric a bleaching composition according to any of the preceding claims and optionally rinsing.

14. Use of a stable composition comprising preformed peroxycarboxylic acid and a metal phthalocyanine colouring agent to bleach fabrics.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 99 87 0133

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Place of search	Date of completion of the search	Examiner
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X : particularly relevant if taken alone
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