



(72) CROPPER, James Dawson, GB

(72) LUPPI, Eduardo Jnr, BR

(72) de MEDEIROS, Ana Claudia Marquezano, BR

(71) UNILEVER PLC, GB

(51) Int.Cl.⁶ C11D 3/06, C11D 3/39, C11D 3/36, C11D 3/33

(30) 1996/06/20 (9602854-8) BR

(54) **AMELIORATIONS CONCERNANT DES COMPOSITIONS DE
BLANCHIMENT**

(54) **IMPROVEMENTS RELATING TO BLEACHING
COMPOSITIONS**

(57) L'invention concerne une composition de blanchiment aqueuse dont le pH se situe entre 1 et 3. Cette composition comprend (a) 0,1 à 15 % en poids de tensio-actif; (b) 3 à 15 % en poids de peroxyde d'hydrogène ou d'une source de ce dernier; (c) 0,5 à 10 % en poids de disodium dihydrogène pyrophosphate; (d) 0,1 à 1 % en poids d'au moins un agent complexant d'ions métalliques autre que (c); et (e) 0,01 à 1 % en poids de parfum. L'invention concerne aussi un procédé pour enlever les taches sur des articles textiles, qui consiste à traiter les articles avec une composition susmentionnée.

(57) The invention relates to an aqueous bleaching composition of pH 1-3 which comprises: a) 0.1-15 w.t.% surfactant; b) 3-15 w.t.% hydrogen peroxide or a source thereof; c) 0.5-10 w.t.% disodium dihydrogen pyrophosphate; d) 0.1-3 w.t.% of at least one metal ion complexing agent other than (c); and e) 0.01-1 w.t.% perfume. The invention also provides a process for removing stains from textile articles which comprises the step of treating the articles with a composition as described above.

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C11D 3/06, 3/39, 3/36, 3/33	A3	(11) International Publication Number: WO 97/48785 (43) International Publication Date: 24 December 1997 (24.12.97)
(21) International Application Number: PCT/EP97/03059 (22) International Filing Date: 10 June 1997 (10.06.97) (30) Priority Data: PI 9602854-8 20 June 1996 (20.06.96) BR (71) Applicant (for AU BB CA GB GH IE IL KE LC LK LS MN MW NZ SD SG SZ TT UG only): UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB). (71) Applicant (for all designated States except AU BB CA GB GH IE IL KE LC LK LS MN MW NZ SD SG SZ TT UG US): UNILEVER N.V. [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL). (72) Inventors; and (75) Inventors/Applicants (for US only): CROPPER, James, Dawson [GB/GB]; 7 Gardens Road, Bebington, Wirral, Merseyside L63 7QZ (GB). LUPPI, Eduardo, Junior [BR/BR]; Apartamento 62, Avenida da Saudade, 159, Campinas, CEP-13041-670 São Paulo (BR). MARQUEZANO DE MEDEIROS, Ana, Claudia [BR/BR]; Apartamento 41, Deolinda Rodrigues, 161, CEP-53372-100 São Paulo (BR).		(74) Agent: ELLIOTT, Peter, William; Unilever plc, Patent Division, Colworth House, Sharnbrook, Bedford MK44 1LQ (GB). (81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i> (88) Date of publication of the international search report: 5 February 1998 (05.02.98)
(54) Title: IMPROVEMENTS RELATING TO BLEACHING COMPOSITIONS (57) Abstract The invention relates to an aqueous bleaching composition of pH 1-3 which comprises: a) 0.1-15 w.t.% surfactant; b) 3-15 w.t.% hydrogen peroxide or a source thereof; c) 0.5-10 w.t.% disodium dihydrogen pyrophosphate; d) 0.1-3 w.t.% of at least one metal ion complexing agent other than (c); and e) 0.01-1 w.t.% perfume. The invention also provides a process for removing stains from textile articles which comprises the step of treating the articles with a composition as described above.		

IMPROVEMENTS RELATING TO BLEACHING COMPOSITIONS5 Technical Field

10 The present invention relates to bleaching compositions, and relates particularly to bleaching compositions which can be used on fabrics either by direct application of the composition to the fabric or as a wash additive.

Background to the Invention

15 In household cleaning, fabric washing and in many other areas there is a general need for agents which can 'bleach' unsightly materials, i.e. which can react with these materials to decolourise them. One of the commonest of such bleaching agents is sodium hypochlorite, which is
20 widely used in cleaning compositions to decolourise soils, to assist in cleaning through its reaction with soils and to kill micro-organisms.

25 Sodium hypochlorite is a powerful oxidising agent, which can decolourise a very large number of coloured compounds found in soils but which has significant limitations. Many consumers prefer not to use chlorine-based bleach compounds due the characteristic and pungent smell of chlorine.

30 There is a need for an alternative to chlorine-based bleaching and bleaching and/or cleaning agents. One well known class of alternatives are the peroxygen compounds. Wash additives based on hydrogen peroxide and other peroxides for laundry applications are well known. These
35 generally comprise a surfactant, a peroxygen bleaching agent and a metal sequestering agent.

- 2 -

WO 9314183 (P&G: 1992) relates to a stable colourless detergent composition of pH 4-11 which comprises:

- 5 a) 5-95%wt of anionic or nonionic surfactant (which can be a nonionic surfactant),
- b) 0.005-10%wt of an oxygen bleach (which can be hydrogen peroxide),
- 10 c) 0.001-8% of a metal sequestering agent (which can be sodium pyrophosphate or a DEQUEST(TM) type sequestering agent).

15 Brief Description of the Invention

We have determined that stable low pH peroxygen bleaching compositions of pH less than 4 can be formulated using disodium dihydrogen pyrophosphate in combination with a
20 second metal-ion complexing agent.

Accordingly, the present invention provides an aqueous bleaching composition of pH 1-3 which comprises:

- 25 a) 0.1-15%wt surfactant
- b) 3-15%wt hydrogen peroxide or a source thereof,
- c) 0.5-10%wt disodium dihydrogen pyrophosphate,
- 30 d) 0.1-3%wt of at least one metal ion complexing agent other than (c), and,
- e) optionally, 0.01-1%wt perfume.

35

- 3 -

The invention also provides a process for removing stains from textile articles which comprises the step of treating the articles with a composition as described herein.

5

Detailed Description of the Invention

Compositions according to the present invention invariably comprise at least 0.5%wt of disodium dihydrogen pyrophosphate (otherwise known as sodium acid pyrophosphate) and have a pH in the range 1-3. The other components present are subject to some variability as to their precise nature and are discussed in further detail below.

15

Surfactants

Preferred compositions according to the present invention comprise 2-8%wt of surfactant on product. A broad range of surfactants and surfactant combinations can be used in the compositions of the invention. Surfactants can be nonionic, anionic, cationic, amphoteric or zwitterionic provided that they, and where appropriate their counter-ions, do not react substantially with any peroxide compounds present. Preferred surfactants are selected from nonionic surfactants, anionic surfactants and mixtures thereof.

25

Suitable nonionic detergent active compounds can be broadly described as compounds produced by the condensation of alkylene oxide groups, which are hydrophillic in nature, with an organic hydrophobic compound which may be aliphatic or alkyl aromatic in nature. The length of the hydrophillic or polyoxyalkylene radical which is condensed with any particular hydrophobic group can be readily

35

- 4 -

adjusted to yield a water-soluble compound having the desired degree of balance between hydrophillic and hydrophobic elements.

5 Particular examples include the condensation product of aliphatic alcohols having from 8 to 22 carbon atoms in either straight or branched chain configuration with ethylene oxide, such as a coconut oil ethylene oxide
10 condensate having from 2 to 10 moles of ethylene oxide per mole of coconut alcohol; condensates of alkylphenols whose alkyl group contains from 6 to 12 carbon atoms with 2 to 10 moles of ethylene oxide per mole of alkylphenol.

15 The preferred alkoxyated alcohol nonionic surfactants are ethoxylated alcohols having a chain length of C12-C15 and an EO value of at least 2 but less than 10. Particularly preferred nonionic surfactants include the condensation products of C₁₂₋₁₅ alcohols with 3-9 moles of ethylene oxide. An example of a suitable surfactant is 'Dobanol 25 7EO'
20 (TM, ex. Shell) a C₁₂₋₁₅ alcohol with seven moles of ethoxylation.

When present, the amount of nonionic detergent active to be employed in the composition of the invention will generally
25 be from 0.1 to 15%wt, preferably from 0.1 to 10%wt, and most preferably from 4 to 10%wt.

We have also found it useful to employ a mixed nonionic surfactant system which comprises two nonionics one of
30 which has a relatively high HLB and the other of which has a relatively low HLB. In aqueous systems this combination of nonionics forms a stable emulsion. An example of a suitable system is one which comprises 2-5%wt each of two C12-C15 alcohols ethoxylated with 2-4 and 6-8 moles of
35 ethylene oxide respectively. Two suitable nonionics are

- 5 -

Dobanol 25 7EO [TM] ex. Shell and Dobanol 25 3EO [TM] ex. Shell.

5 Alternative surfactants include amine oxides, amines and/or ethoxylates thereof. Amine oxides with a carbon chain length of C12-C14 are particularly preferred.

10 Suitable anionic detergent active compounds are water-soluble salts of organic sulphuric reaction products having in the molecular structure an alkyl radical containing from 8 to 22 carbon atoms, and a radical chosen from sulphonic acid or sulphur acid ester radicals and mixtures thereof.

15 Examples of suitable anionic detergents are sodium and potassium alcohol sulphates, especially those obtained by sulphating the higher alcohols produced by reducing the glycerides of tallow or coconut oil; sodium and potassium alkyl benzene sulphonates such as those in which the alkyl group contains from 9 to 15 carbon atoms; sodium and
20 potassium secondary alkanesulphonates; sodium alkyl glyceryl ether sulphates, especially those ethers of the higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulphates; sodium and potassium salts of sulphuric acid esters of the reaction
25 product of one mole of a higher fatty alcohol and from 1 to 6 moles of ethylene oxide; sodium and potassium salts of alkyl phenol ethylene oxide ether sulphate with from 1 to 8 units of ethylene oxide molecule and in which the alkyl radicals contain from 4 to 14 carbon atoms; the reaction
30 product of fatty acids esterified with isethionic acid and neutralised with sodium hydroxide where, for example, the fatty acids are derived from coconut oil and mixtures thereof.

35 The preferred water-soluble synthetic anionic detergent active compounds are the alkali metal (such as sodium and

- 6 -

potassium) and alkaline earth metal (such as calcium and magnesium) salts of higher alkyl benzene sulphonates and mixtures with olefinsulphonates and higher alkyl sulphates, and the higher fatty acid monoglyceride sulphates.

5

The most preferred anionic detergent active compounds are higher alkyl aromatic sulphonates (LAS) such as higher alkyl benzene sulphonates containing from 6 to 20 carbon atoms in the alkyl group in a straight or branched chain, particular examples of which are sodium salts of higher alkyl benzene sulphonates or of higher-alkyl toluene, xylene or phenol sulphonates, alkyl naphthalene sulphonates, ammonium diethyl naphthalene sulphonate, and sodium dinonyl naphthalene sulphonate. The most preferred anionics also include the higher alcohol sulphates (also known as alkyl sulphates) containing from 6 to 20 carbon atoms in the alkyl group in a straight or branched chain, particular examples of which are sodium salts of higher primary alkyl sulphates (PAS).

15
20

The amount of synthetic anionic detergent active to be employed in the detergent composition of this invention will generally be from 0.1 to 15%, preferably from 1 to 5%wt, with levels of 1-2%wt being particularly preferred.

25

Preferably, the compositions contain an amount of both the anionic and the nonionic detergent active. Preferably the total surfactant content lies in the range 0.1-10%wt.

30

The weight ratio of anionic detergent to nonionic detergent active may vary and will depend on their nature but is preferably in the range of from 1:9 to 9:1, ideally from 1:4 to 4:1. We have determined that a particularly suitable surfactant system comprises 1-2% alkyl benzene sulphonate and 0.5-2%wt C12-15, 5-8 EO ethoxylated alcohol nonionic, a suitable alternative surfactant system

35

- 7 -

comprises 1-2%wt of primary alcohol sulphate (also known as primary alkyl sulphate) and 0.5-2%wt C12-15, 5-8 EO ethoxylated alcohol nonionic.

5

Peroxide

Suitable peroxy compounds for inclusion in compositions according to the invention include, hydrogen peroxide, perborates, persulphates, peroxysulphates, perphosphates, periodates, percarbonates and mixtures thereof.

Particularly preferred materials are hydrogen peroxide, sodium peroxide, peracetic acid, performic acid and mono-persulphate salts. Hydrogen peroxide is most preferred.

15

Preferred compositions according to the present invention comprise 5-10%wt hydrogen peroxide,

20

Metal ion complexing agents

Preferred compositions according to the present invention comprise 1-7%wt, more preferably 1-2%wt disodium dihydrogen pyrophosphate. This material is otherwise known as sodium acid pyrophosphate.

25

Preferred compositions according to the present invention comprise 0.1-0.5%wt of at least one metal ion complexing agent other than disodium dihydrogen pyrophosphate,

30

Preferably, cleaning and/or disinfecting compositions according to the invention will further comprise metal ion sequestrants such as ethylene-diamine-tetra-acetates, amino-polyphosphonates (such as those in the DEQUEST (TM) range) and phosphates and a wide variety of other poly-

35

- 8 -

functional organic acids and salts, can also optionally be employed.

5 Preferred metal ion sequesterants are selected from
dipicolinic acid, ethylene diamine tetra acetic acid (EDTA)
and its salts, hydroxy-ethylidene diphosphonic acid
(Dequest 2010, RTM), ethylene diamine tetra (methylene
phosphonic acid) (Dequest 2040, RTM), diethylene triamine
10 penta(methylene phosphonic acid) (Dequest 2060, RTM), amino
tri(methylene phosphonic acid) (Dequest 2000, RTM).

The phosphonic acid derivatives are particularly preferred.
Diethylene triamine penta(methylene phosphonic acid)
(Dequest 2060, RTM) is particularly preferred.

15 It is preferred that the level of phosphonic acid
derivative metal ion complexing agent should fall into the
range 0.1-3%wt, with levels of 0.1-0.5%wt being
particularly preferred.

20

Perfumes

25 Perfume is an optional component of the present invention
but is highly preferred. Preferred compositions according
to the present invention comprise 0.1-0.2%wt of perfume. A
wide range of perfumes can be employed provided that the
perfume is sufficiently stable in the composition.

30

Other Minors

Where compositions according to the present invention are
liquids, they can be water-thin or thickened. Thickened
35 compositions are advantageous in that they cling to sloping
surfaces and find particular utility in toilet cleaners.

- 9 -

5 Slight thickening of the composition is desirable for applications in which the composition is sprayed, so as to reduce the extent to which small droplets are produced which might otherwise cause respiratory irritation to the user. Suitable thickening agents include amine oxide and soap and systems based on nonionic surfactants. Preferably the compositions are no significantly thickened.

10 Compositions according to the invention can also contain, in addition to the ingredients already mentioned, various other optional ingredients such as, colourants, optical brighteners, soil suspending agents, gel-control agents, freeze-thaw stabilisers and opacifiers.

15 Preferably the pH of compositions according to the invention is in the range 1.5-2.5. The pH of compositions according to the invention can be regulated using acids, preferably HCl and alkali's, preferably NaOH.

20 In order that the invention can be further understood it will be described hereafter with reference to the following non-limiting examples.

25 **Examples**

The following compositions (as shown in table 2) were made up using materials as identified in table 1.

30

- 10 -

Table 1

Material	Sold as	Supplier
C12-15/7EO	Dobanol 25 7EO(TM)	Shell
C12-15/3EO	Dobanol 25 3EO(TM)	Shell
PAS	Dacapon (TM)	Unger
LAS (acid form)	Made in house	Lever Brothers
NaOH	Caustic soda 47%	ICI
Sequesterant	Dequest 2060S(TM)	Monsanto
Na ₂ H ₂ pyrophosphate	-	Albright & Wilson
Perfume	BAX 47867	IFF

The compositions were prepared by mixing the compounds as indicating below in a stirring tank at room temperature.. No particular order of addition is required, although it is preferred that the perfume and any dyestuff are added last.

- 11 -

Table 2

Comp	A	B	C	D
C12-15/7EO	3.5%	1.0%	7.0%	1.0%
C12-15/3EO	3.5%	-	-	-
PAS	-	1.5%	-	-
LAS (acid form)	-	-	-	1.5%
NaOH	-	-	-	0.176%
HCl	0.0215%	0.0215%	0.0215%	0.0215%
Sequesterant	0.15%	0.15%	0.15%	0.15%
H2O2	7.0%	7.0%	7.0%	7.0%
Na ₂ H ₂ pyrophosphate	1.8%	1.8%	1.8%	1.8%
Perfume	0.15%	0.15%	0.15%	0.15%
Colour	0.0008%	0.0008%	0.0008%	0.0008%
Water	to 100%	to 100%	to 100%	to 100%
pH	2.12	2.00	2.10	1.93

All were found to be stable compositions which showed acceptable bleaching behaviour when used as wash additives and in direct application to soiled articles.

Claims

- 5 1. An aqueous bleaching composition of pH 1-3 which
 comprises:
- a) 0.1-15%wt surfactant
- 10 b) 3-15%wt of a peroxy compound selected from:
 hydrogen peroxide, perborates, persulphates,
 peroxysulphates, perphosphates, periodates,
 percarbonates, sodium peroxide, peracetic acid,
 performic acid and mixtures thereof,
- 15 c) 0.5-10%wt disodium dihydrogen pyrophosphate,
- d) 0.1-3%wt of at least one metal ion complexing
 agent other than (c), and,
- 20 e) optionally, 0.01-1%wt perfume.
2. Composition according to claim 1 which comprises 2-
 5%wt of each of two C12-C15 alcohols ethoxylated with
25 2-4 and 6-8 moles of ethylene oxide respectively.
3. Composition according to claim 1 which comprises a
 surfactant selected from the group comprising alkyl
 benzene sulphonate containing from 6 to 20 carbon
30 atoms in the alkyl group in a straight or branched
 chain and alkyl sulphates containing from 6 to 20
 carbon atoms in the alkyl group in a straight or
 branched chain.

4. Composition according to claim 1 wherein the amount of
5 synthetic anionic detergent active in the composition
is from 1-2%wt.
5. Composition according to any preceding claim which
comprises both anionic and nonionic detergent active.
- 10 6. Composition according to any preceding claim wherein
the at least one metal ion complexing agent other than
disodium dihydrogen pyrophosphate is selected from the
group comprising: ethylene diamine tetra acetic acid
15 and its salts, hydroxy-ethylidene diphosphonic acid,
ethylene diamine tetra (methylene phosphonic acid),
diethylene triamine penta(methylene phosphonic acid),
and, amino tri(methylene phosphonic acid).
- 20 7. Composition according to any preceding claim wherein
the at least one metal ion complexing agent other than
disodium dihydrogen pyrophosphate is a phosphonic acid
derivative and the level of phosphonic acid derivative
metal ion complexing agent falls into the range 0.1-
25 0.5%wt.
8. Composition according to any preceding claim wherein
the pH of compositions is in the range 1.5-2.5.
- 30 9. Composition according to any preceding claim which
comprises hydrogen peroxide.

10. A process for removing stains from textile articles
which comprises the step of treating the articles with
5 a composition according to any one of claims 1-9
either in neat or dilute form.