

(19)



(11)

EP 2 292 725 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

09.03.2011 Bulletin 2011/10

(51) Int Cl.:

C11D 11/00 (2006.01) **C11D 3/00** (2006.01)
C11D 3/39 (2006.01) **C11D 3/34** (2006.01)
C11D 3/16 (2006.01) **C11D 3/386** (2006.01)
C11D 1/29 (2006.01)

(21) Application number: **09010447.2**

(22) Date of filing: **13.08.2009**

(84) Designated Contracting States:

**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL
PT RO SE SI SK SM TR**

Designated Extension States:

AL BA RS

(71) Applicant: **The Procter & Gamble Company**
Cincinnati, OH 45202 (US)

(72) Inventor: **Souter, Philp Frank**

Morpeth, Northumberland NE65 8UP (GB)

(74) Representative: **Howard, Phillip Jan et al**

Procter & Gamble
Technical Centres Limited
Whitley Road
Longbenton
Newcastle upon Tyne NE12 9TS (GB)

(54) **Method of laundering fabrics at low temperature**

(57) The present invention relates to a method of laundering fabric comprising the step of contacting a laundry detergent composition to water to form a wash liquor, and laundering fabric in said wash liquor, wherein the wash liquor has a temperature of above 0°C to 20°C,

and wherein the laundry detergent composition comprises greater than 1wt% deterative surfactant and other detergent ingredients.

EP 2 292 725 A1

Description

FIELD OF THE INVENTION

5 **[0001]** The present invention relates to a method of laundering fabric. The method exhibits good fabric cleaning performance, good fabric care profile, good fabric freshness profile, and has an excellent environmental profile.

BACKGROUND OF THE INVENTION

10 **[0002]** With the move to more environmentally friendly and sustainable laundry products, laundering processes, and laundry washing machine applications, there is a need to ensure that the fabric cleaning, fabric care and fabric freshness profiles remain acceptable. With lower wash temperatures, the dissolution performance is impaired, especially of solid laundry detergent products. In addition, the reaction kinetics of the laundering processes are reduced with lower wash temperatures. The fabric deposition performance is also affected by lowering the wash temperature. The perfume release
15 profile also changes with lowering wash temperatures.

[0003] The inventors have found that certain detergent ingredients, and certain combinations of detergent ingredients enable low temperature laundering of fabric in a more environmentally friendly and sustainable manner, whilst ensuring good fabric cleaning performance, good fabric care profile, and good fabric freshness profile.

20 SUMMARY OF THE INVENTION

[0004] The present invention relates to a method of laundering fabric as defined by the claims.

DETAILED DESCRIPTION OF THE INVENTION

25

Method of laundering fabric

[0005] The method of laundering fabric comprises the step of contacting a laundry detergent composition to water to form a wash liquor, and laundering fabric in said wash liquor, wherein the wash liquor has a temperature of above 0°C
30 to 20°C, preferably to 19 °C, or to 18 °C, or to 17°C, or to 16°C, or to 15 °C, or to 14 °C, or to 13 °C, or to 12 °C, or to 11 °C, or to 10 °C, or to 9 °C, or to 8 °C, or to 7 °C, or to 6 °C, or even to 5°C. The fabric may be contacted to the water prior to, or after, or simultaneous with, contacting the laundry detergent composition with water.

[0006] Typically, the wash liquor is formed by contacting the laundry detergent to water in such an amount so that the concentration of laundry detergent composition in the wash liquor is from above 0g/l to 5g/l, preferably from 1g/l, and
35 preferably to 4.5g/l, or to 4.0g/l, or to 3.5g/l, or to 3.0g/l, or to 2.5g/l, or even to 2.0g/l, or even to 1.5g/l.

[0007] Highly preferably, the method of laundering fabric is carried out in a front-loading automatic washing machine. In this embodiment, the wash liquor formed and concentration of laundry detergent composition in the wash liquor is that of the main wash cycle. Any input of water during any optional rinsing step(s) that typically occurs when laundering fabric using a front-loading automatic washing machine is not included when determining the volume of the wash liquor.
40 Of course, any suitable automatic washing machine may be used, although it is extremely highly preferred that a front-loading automatic washing machine is used.

[0008] It is highly preferred for the wash liquor to comprise 40 litres or less of water, preferably 35 litres or less, preferably 30 litres or less, preferably 25 litres or less, preferably 20 litres or less, preferably 15 litres or less, preferably 12 litres or less, preferably 10 litres or less, preferably 8 litres or less, or even 6 litres or less of water. Preferably, the
45 wash liquor comprises from above 0 to 15 litres, or from 1 litre, or from 2 litres, or from 3 litres, and preferably to 12 litres, or to 10 litres, or even to 8 litres of water. Most preferably, the wash liquor comprises from 1 litre, or from 2 litres, or from 3 litres, or from 4 litres, or even from 5 litres of water.

[0009] Typically from 0.01kg to 2kg of fabric per litre of wash liquor is dosed into said wash liquor. Typically from 0.01kg, or from 0.02kg, or from 0.03kg, or from 0.05kg, or from 0.07kg, or from 0.10kg, or from 0.12kg, or from 0.15kg,
50 or from 0.18kg, or from 0.20kg, or from 0.22kg, or from 0.25kg fabric per litre of wash liquor is dosed into said wash liquor.

[0010] Preferably 50g or less, more preferably 45g or less, or 40g or less, or 35g or less, or 30g or less, or 25g or less, or 20g or less, or even 15g or less, or even 10g or less of laundry detergent composition is contacted to water to form the wash liquor.

[0011] Preferably, the laundry detergent composition is contacted to from above 0 litres, preferably from above 1 litre, and preferably to 70 litres or less of water to form the wash liquor, or preferably to 40 litres or less of water, or preferably to 35 litres or less, or preferably to 30 litres or less, or preferably to 25 litres or less, or preferably to 20 litres or less, or preferably to 15 litres or less, or preferably to 12 litres or less, or preferably to 10 litres or less, or preferably to 8 litres
55 or less, or even to 6 litres or less of water to form the wash liquor.

[0012] Especially preferably, catalytic ingredients are used to improve the cleaning performance of the laundry detergent composition during the process of the present invention. Catalytic ingredients are also preferably used to improve the hygiene profile of the laundry detergent composition during the method of the present invention.

Laundry detergent composition

[0013] The laundry detergent composition comprises and wherein the laundry detergent composition comprises greater than 1wt% deterative surfactant and other detergent ingredients.

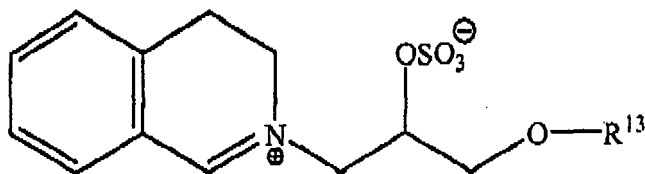
[0014] The composition can be any form, for example a solid powder or tablet form, or a liquid including gel form, or any combination thereof. The composition may be in any unit dose form, for example a tablet or a pouch, or even a detergent sheet. However, it is extremely highly preferred for the composition to be in solid form, and it is especially preferred for the composition to be in a solid free-flowing particulate form, for example such that the composition is in the form of separate discrete particles.

[0015] The laundry detergent composition may comprise from 0wt% to 40wt%, or from above 0wt%, and preferably to 30wt%, or to 25wt%, or to 20wt%, or to 15wt%, or to 10wt%, or to 8wt, or to 6wt%, or to 4wt%, or to 2wt% water. This may be preferred if the composition is in liquid including gel form, and/or unit dose form such as a unit dose pouch.

[0016] The composition is a fully finished laundry detergent composition. Typically, if the composition is in free-flowing particulate form, the composition comprises a plurality of chemically different particles populations. The composition is not just a component of a laundry detergent composition that can be incorporated into a laundry detergent composition (such as an enzyme pill, or a surfactant particle, or a bleach particle), it is a fully finished laundry detergent composition. That said, it is within the scope of the present invention for an additional rinse additive composition (e.g. fabric conditioner or enhancer), or a main wash additive composition (e.g. bleach additive) to also be used in combination with the laundry detergent composition during the method of the present invention. Although, it may be preferred for no bleach additive composition is used in combination with the laundry detergent composition during the method of the present invention.

[0017] The laundry detergent composition preferably comprises from 0wt% to less than 10wt% zeolite builder, and from 0wt% to less than 10wt% phosphate builder. The laundry detergent composition may comprise cationic polymer. The laundry detergent composition may preferably comprise perfume microcapsule.

[0018] A highly preferred laundry detergent composition is a solid laundry detergent composition comprising: (a) alkyl ethoxylated sulphate having an average degree of ethoxylation of from 0.5 to 3.5; (b) from 0wt% to 10wt% zeolite builder; (c) from 0wt% to 10wt% phosphate builder; (d) enzyme; (e) bleach catalyst having a structure corresponding to general formula below:



wherein R^{13} is selected from the group consisting of 2-ethylhexyl, 2-propylheptyl, 2-butyloctyl, 2-pentylnonyl, 2-hexyldecyl, n-dodecyl, n-tetradecyl, n-hexadecyl, n-octadecyl, iso-nonyl, iso-decyl, iso-tridecyl and iso-pentadecyl; (f) layered particle, wherein the layered particle comprises a core and a layer, wherein the core comprises a source of hydrogen peroxide, wherein the layer comprises a binder and a bleach activator, and wherein the weight ratio of the source of hydrogen peroxide to the bleach activator is from about 5:1 to about 1.1:1; (g) optionally, transition metal bleach catalyst; (h) optionally, hueing agent; and (i) optionally, from 0wt% to 10wt% sodium carbonate.

Bleach ingredient

[0019] Preferably the laundry detergent composition comprises a bleach ingredient, the bleach ingredient has a $\log P_{o/w}$ no greater than 0, preferably no greater than -0.5, preferably no greater than -1.0, preferably no greater than -1.5, preferably no greater than -2.0, preferably no greater than -2.5, preferably no greater than -3.0, even more preferably no greater than -3.5. The method for determining $\log P_{o/w}$ is described in more detail below.

[0020] Typically, the bleach ingredient is capable of generating a bleaching species having a X_{SO} of from 0.01 to about 0.30, preferably from 0.05 to about 0.25, even more preferably from about 0.10 to 0.20. The method for determining X_{SO} is described in more detail below. For example, bleaching ingredients having an isoquinolinium structure are capable

of generating a bleaching species that has an oxaziridinium structure. In this example, the X_{SO} is that of the oxaziridinium bleaching species.

[0021] Without wishing to be bound by theory, the inventors believe that controlling the electrophilicity and hydrophobicity in this above described manner enables the bleach ingredient to be delivered substantially only to areas of the fabric that are more hydrophobic, and that contain electron rich soils, including visible chromophores, that are susceptible to bleaching by highly electrophilic oxidants.

[0022] Preferably, the bleaching ingredient is catalytic. A highly preferred bleach ingredient is a bleach catalyst that is capable of accepting an oxygen atom from a peroxyacid and/or salt thereof, and transferring the oxygen atom to an oxidizable substrate. Suitable bleach catalysts include, but are not limited to: iminium cations and polyions; iminium zwitterions; modified amines; modified amine oxides; N-sulphonyl imines; N-phosphonyl imines; N-acyl imines; thiadiazole dioxides; perfluoroimines; cyclic sugar ketones and mixtures thereof.

[0023] Suitable iminium cations and polyions include, but are not limited to, N-methyl-3,4-dihydroisoquinolinium tetrafluoroborate, prepared as described in Tetrahedron (1992), 49(2), 423-38 (see, for example, compound 4, p. 433); N-methyl-3,4-dihydroisoquinolinium p-toluene sulphonate, prepared as described in U.S. Pat. 5,360,569 (see, for example, Column 11, Example 1); and N-octyl-3,4-dihydroisoquinolinium p-toluene sulphonate, prepared as described in U.S. Pat. 5,360,568 (see, for example, Column 10, Example 3).

[0024] Suitable iminium zwitterions include, but are not limited to, N-(3-sulfoethyl)-3,4-dihydroisoquinolinium, inner salt, prepared as described in U.S. Pat. 5,576,282 (see, for example, Column 31, Example II); N-[2-(sulphooxy)dodecyl]-3,4-dihydroisoquinolinium, inner salt, prepared as described in U.S. Pat. 5,817,614 (see, for example, Column 32, Example V); 2-[3-[(2-ethylhexyl)oxy]-2-(sulphooxy)propyl]-3,4-dihydroisoquinolinium, inner salt, prepared as described in WO05/047264 (see, for example, page 18, Example 8), and 2-[3-[(2-butyloctyl)oxy]-2-(sulphooxy)propyl]-3,4-dihydroisoquinolinium, inner salt.

[0025] Suitable modified amine oxygen transfer catalysts include, but are not limited to, 1,2,3,4-tetrahydro-2-methyl-1-isoquinolinol, which can be made according to the procedures described in Tetrahedron Letters (1987), 28(48), 6061-6064. Suitable modified amine oxide oxygen transfer catalysts include, but are not limited to, sodium 1-hydroxy-N-oxy-N-[2-(sulphooxy)decyl]-1,2,3,4-tetrahydroisoquinoline.

[0026] Suitable N-sulphonyl imine oxygen transfer catalysts include, but are not limited to, 3-methyl-1,2-benzisothiazole 1,1-dioxide, prepared according to the procedure described in the Journal of Organic Chemistry (1990), 55(4), 1254-61.

[0027] Suitable N-phosphonyl imine oxygen transfer catalysts include, but are not limited to, [R-(E)]-N-[(2-chloro-5-nitrophenyl)methylene]-P-phenyl-P-(2,4,6-trimethylphenyl)-phosphinic amide, which can be made according to the procedures described in the Journal of the Chemical Society, Chemical Communications (1994), (22), 2569-70.

[0028] Suitable N-acyl imine oxygen transfer catalysts include, but are not limited to, [N(E)]-N-(phenylmethylene)acetamide, which can be made according to the procedures described in Polish Journal of Chemistry (2003), 77(5), 577-590.

[0029] Suitable thiadiazole dioxide oxygen transfer catalysts include but are not limited to, 3-methyl-4-phenyl-1,2,5-thiadiazole 1,1-dioxide, which can be made according to the procedures described in U.S. Pat. 5,753,599 (Column 9, Example 2).

[0030] Suitable perfluoroimine oxygen transfer catalysts include, but are not limited to, (Z)-2,2,3,3,4,4,4-heptafluoro-N-(nonafluorobutyl)butanimidoyl fluoride, which can be made according to the procedures described in Tetrahedron Letters (1994), 35(34), 6329-30.

[0031] Suitable cyclic sugar ketone oxygen transfer catalysts include, but are not limited to, 1,2:4,5-di-O-isopropylidene-D-erythro-2,3-hexodiuro-2,6-pyranose as prepared in U.S. Pat. 6,649,085 (Column 12, Example 1).

[0032] Preferably, the bleach catalyst comprises an iminium and/or carbonyl functional group and is typically capable of forming an oxaziridinium and/or dioxirane functional group upon acceptance of an oxygen atom, especially upon acceptance of an oxygen atom from a peroxyacid and/or salt thereof. Preferably, the bleach catalyst comprises an oxaziridinium functional group and/or is capable of forming an oxaziridinium functional group upon acceptance of an oxygen atom, especially upon acceptance of an oxygen atom from a peroxyacid and/or salt thereof. Preferably, the bleach catalyst comprises a cyclic iminium functional group, preferably wherein the cyclic moiety has a ring size of from five to eight atoms (including the nitrogen atom), preferably six atoms. Preferably, the bleach catalyst comprises an aryliminium functional group, preferably a bi-cyclic aryliminium functional group, preferably a 3,4-dihydroisoquinolinium functional group. Typically, the imine functional group is a quaternary imine functional group and is typically capable of forming a quaternary oxaziridinium functional group upon acceptance of an oxygen atom, especially upon acceptance of an oxygen atom from a peroxyacid and/or salt thereof.

[0033] Preferably, the bleach catalyst has a chemical structure corresponding to the following chemical formula:



15

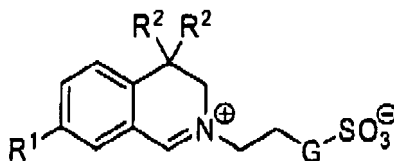
25

35



50

55



wherein: G is selected from -O-, -CH₂O-, -(CH₂)₂-, and -CH₂-. R¹ is selected from H or C₁-C₄ alkyl. Suitable C₁-C₄ alkyl moieties include, but are not limited to methyl, ethyl, iso-propyl, and tert-butyl. Each R² is independently selected from C₄-C₈ alkyl, benzyl, 2-methylbenzyl, 3-methylbenzyl, 4-methylbenzyl, 4-ethylbenzyl, 4-iso-propylbenzyl and 4-tert-butylbenzyl. Suitable C₄-C₈ alkyl moieties include, but are not limited to n-butyl, n-pentyl, cyclopentyl, n-hexyl, cyclohexyl, cyclohexylmethyl, n-heptyl and octyl.

[0036] In one aspect of the invention G is selected from -O- and -CH₂-. R¹ is selected from H, methyl, ethyl, iso-propyl, and tert-butyl. Each R² is independently selected from C₄-C₆ alkyl, benzyl, 2-methylbenzyl, 3-methylbenzyl, and 4-methylbenzyl.

[0037] In another aspect of the invention G is -CH₂-, R¹ is H and each R² is independently selected from n-butyl, n-pentyl, n-hexyl, benzyl, 2-methylbenzyl, 3-methylbenzyl, and 4-methylbenzyl.

Method of determining logP_{o/w}

[0038] Log P_{o/w} is determined according to the method found in Brooke, D. N., Dobbs, A. J., Williams, N, Ecotoxicology and Environmental Safety (1986) 11(3): 251-260.

Method of determining X_{so}

[0039] The parameter X_{so} is determined according to the method described in Adam, W., Haas, W., Lohray, B. B. Journal of the American Chemical Society (1991) 113(16) 6202-6208.

Transition metal bleach catalyst

[0040] Preferably, the laundry detergent composition comprises a transition metal catalyst. Preferably, the transition metal catalyst may be encapsulated. The transition metal bleach catalyst typically comprises a transition metal ion, preferably selected from transition metal selected from the group consisting of Mn(II), Mn(III), Mn(IV), Mn(V), Fe(II), Fe(III), Fe(IV), Co(I), Co(II), Co(III), Ni(I), Ni(II), Ni(III), Cu(I), Cu(II), Cu(III), Cr(II), Cr(III), Cr(IV), Cr(V), Cr(VI), V(III), V(IV), V(V), Mo(IV), Mo(V), Mo(VI), W(IV), W(V), W(VI), Pd(II), Ru(II), Ru(III), and Ru(IV), more preferably Mn(II), Mn(III), Mn(IV), Fe(II), Fe(III), Cr(II), Cr(III), Cr(IV), Cr(V), and Cr(VI).

[0041] The transition metal bleach catalyst typically comprises a ligand, preferably a macropolycyclic ligand, more preferably a cross-bridged macropolycyclic ligand. The transition metal ion is preferably coordinated with the ligand. Preferably, the ligand comprises at least four donor atoms, at least two of which are bridgehead donor atoms.

[0042] Preferably, the cross-bridged macropolycyclic ligand is coordinated by four or five donor atoms to the same transition metal and comprises:

(i) an organic macrocycle ring containing four or more donor atoms selected from N and optionally O and S, at least two of these donor atoms being N (preferably at least 3, more preferably at least 4, of these donor atoms are N), separated from each other by covalent linkages of 2 or 3 non-donor atoms, two to five (preferably three to four, more preferably four) of these donor atoms being coordinated to the same transition metal in the complex;

(ii) a cross-bridging chain which covalently connects at least 2 non-adjacent N donor atoms of the organic macrocycle ring, said covalently connected non-adjacent N donor atoms being bridgehead N donor atoms which are coordinated to the same transition metal in the complex, and wherein said cross-bridged chain comprises from 2 to about 10 atoms (preferably the cross-bridged chain is selected from 2, 3 or 4 non-donor atoms, and 4-6 non-donor atoms with a further, preferably N, donor atom); and

(iii) optionally, one or more non-macropolycyclic ligands, preferably selected from the group consisting of H₂O, ROH, NR₃, RCN, OH⁻, OOH⁻, RS⁻, RO⁻, RCOO⁻, OCN⁻, SCN⁻, N₃⁻, CN⁻, F⁻, Cl⁻, Br⁻, I⁻, O₂⁻, NO₃⁻, NO₂⁻, SO₄²⁻, SO₃²⁻, PO₄³⁻, organic phosphates, organic phosphonates, organic sulfates, organic sulfonates, and aromatic N donors such as pyridines, pyrazines, pyrazoles, imidazoles, benzimidazoles, pyrimidines, triazoles and thiazoles with R being H, optionally substituted alkyl, optionally substituted aryl.

[0043] A suitable transition metal bleach catalyst comprises a complex of a transition metal and a macropolycyclic rigid ligand, preferably a cross-bridged macropolycyclic ligand, wherein:

(1) said transition metal is elected from the group consisting of Mn(II), Mn(III), Mn(IV), Mn(V), Fe(II), Fe(III), Fe(IV), Co(I), Co(II), Co(III), Ni(I), Ni(II), Ni(III), Cu(I), Cu(II), Cu(III), Cr(II), Cr(III), Cr(IV), Cr(V), Cr(VI), V(III), V(IV), V(V), Mo(IV), Mo(V), Mo(VI), W(IV), W(V), W(VI), Pd(II), Ru(II), Ru(III), and Ru(IV); and

(2) said macropolycyclic rigid ligand is coordinated by at least four, preferably four or five, donor atoms to the same transition metal and comprises:

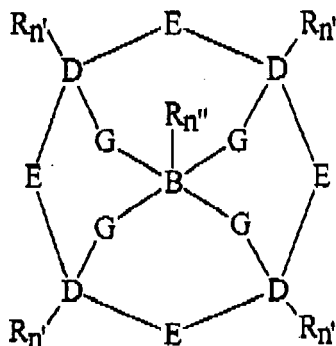
(i) an organic macrocycle ring containing four or more donor atoms (preferably at least 3, more preferably at least 4, of these donor atoms are N) separated from each other by covalent linkages of at least one, preferably 2 or 3, non-donor atoms, two to five (preferably three to four, more preferably four) of these donor atoms being coordinated to the same transition metal in the complex;

(ii) a linking moiety, preferably a cross-bridging chain, which covalently connects at least 2 (preferably non-adjacent) donor atoms of the organic macrocycle ring, said covalently connected (preferably non-adjacent) donor atoms being bridgehead donor atoms which are coordinated to the same transition metal in the complex, and wherein said linking moiety (preferably a cross-bridged chain) comprises from 2 to about 10 atoms (preferably the cross-bridged chain is selected from 2, 3 or 4 non-donor atoms, and 4-6 non-donor atoms with a further donor atom), including for example, a cross-bridge which is the result of a Mannich condensation of ammonia and formaldehyde; and

(iii) optionally, one or more non-macropolycyclic ligands, preferably monodentate ligands, such as those selected from the group consisting of H₂O, ROH, NR₃, RCN, OH⁻, OOH⁻, RS⁻, RO⁻, RCOO⁻, OCN⁻, SCN⁻, N₃⁻, CN⁻, F⁻, Cl⁻, Br⁻, I⁻, O₂⁻, NO₃⁻, NO₂⁻, SO₄²⁻, SO₃²⁻, PO₄³⁻, organic phosphates, organic phosphonates, organic sulfates, organic sulfonates, and aromatic N donors such as pyridines, pyrazines, pyrazoles, imidazoles, benzimidazoles, pyrimidines, triazoles and thiazoles with R being H, optionally substituted alkyl, optionally substituted aryl (specific examples of monodentate ligands including phenolate, acetate or the like).

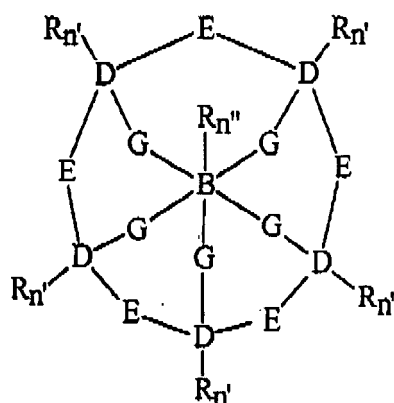
[0044] Suitable cross-bridged macropolycyclic ligands include:

(i) the cross-bridged macropolycyclic ligand of formula (I) having denticity of 4 or 5:



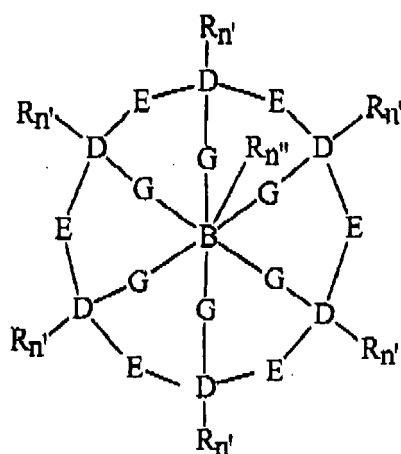
(I);

(ii) the cross-bridged macropolycyclic ligand of formula (II) having denticity of 5 or 6:



(II);

(iii) the cross-bridged macropolycyclic ligand of formula (III) having denticity of 6 or 7:



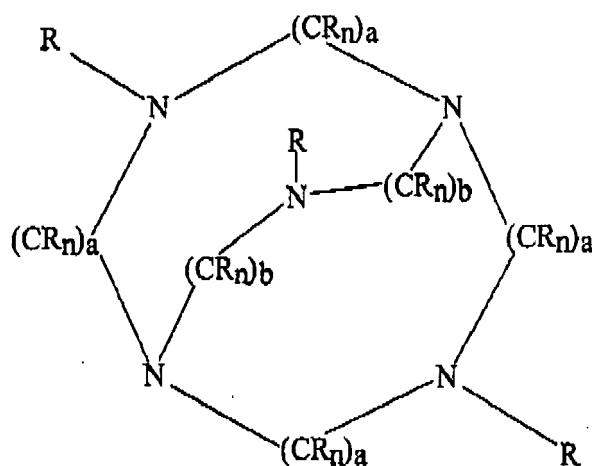
(III);

wherein in these formulas:

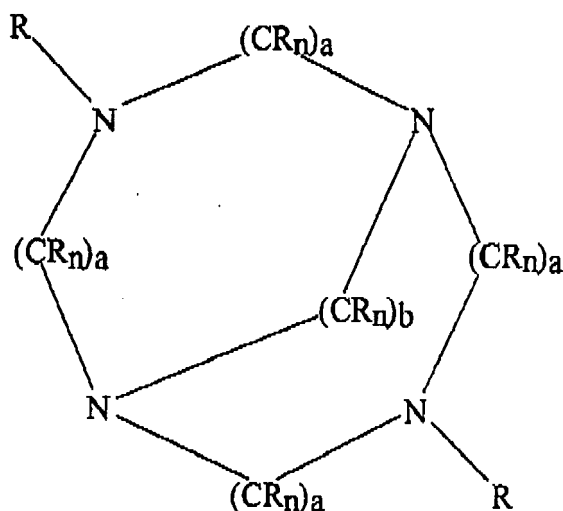
- each "E" is the moiety $(CR_n)_a-X-(CR_n)_{a'}$, wherein -X- is selected from the group consisting of O, S, NR and P, or a covalent bond, and preferably X is a covalent bond and for each E the sum of $a + a'$ is independently selected from 1 to 5, more preferably 2 and 3;
- each "G" is the moiety $(CR_n)_b$;
- each "R" is independently selected from H, alkyl, alkenyl, alkynyl, aryl, alkylaryl (e.g., benzyl), and heteroaryl, or two or more R are covalently bonded to form an aromatic, heteroaromatic, cycloalkyl, or heterocycloalkyl ring;
- each "D" is a donor atom independently selected from the group consisting of N, O, S, and P, and at least two D atoms are bridgehead donor atoms coordinated to the transition metal (in the preferred embodiments, all donor atoms designated D are donor atoms which coordinate to the transition metal, in contrast with heteroatoms in the structure which are not in D such as those which may be present in E; the non-D heteroatoms can be non-coordinating and indeed are non-coordinating whenever present in the preferred embodiment);

- "B" is a carbon atom or "D" donor atom, or a cycloalkyl or heterocyclic ring;
- each "n" is an integer independently selected from 1 and 2, completing the valence of the carbon atoms to which the R moieties are covalently bonded;
- each "n'" is an integer independently selected from 0 and 1, completing the valence of the D donor atoms to which the R moieties are covalently bonded;
- each "n'' is an integer independently selected from 0, 1, and 2 completing the valence of the B atoms to which the R moieties are covalently bonded;
- each "a" and "a'" is an integer independently selected from 0-5, preferably $a + a'$ equals 2 or 3, wherein the sum of all "a" plus "a'" in the ligand of formula (I) is within the range of from about 6 (preferably 8) to about 12, the sum of all "a" plus "a'" in the ligand of formula (II) is within the range of from about 8 (preferably 10) to about 15, and the sum of all "a" plus "a'" in the ligand of formula (III) is within the range of from about 10 (preferably 12) to about 18;
- each "b" is an integer independently selected from 0-9, preferably 0-5 (wherein when $b=0$, $(CR_n)_0$ represents a covalent bond), or in any of the above formulas, one or more of the $(CR_n)_b$ moieties covalently bonded from any D to the B atom is absent as long as at least two $(CR_n)_b$ covalently bond two of the D donor atoms to the B atom in the formula, and the sum of all "b" is within the range of from about 1 to about 5.

[0045] A suitable cross-bridged macropolycyclic ligand is selected from the group consisting of:



(I), and



(II),

wherein in these formulas:

- each "R" is independently selected from H, alkyl, alkenyl, alkynyl, aryl, alkylaryl (e.g., benzyl) and heteroaryl, or two or more R are covalently bonded to form an aromatic, heteroaromatic, cycloalkyl, or heterocycloalkyl ring;
- each "n" is an integer independently selected from 0, 1 and 2, completing the valence of the carbon atoms to which the R moieties are covalently bonded;
- each "b" is an integer independently selected from 2 and 3; and
- each "a" is an integer independently selected from 2 and 3.

Suitable transition metal bleach catalysts include: Dichloro-5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(II); Dichloro-4,10-dimethyl-1,4,7,10-tetraazabicyclo[5.5.2]tetradecane Manganese(II); Diaquo-5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(II) Hexafluorophosphate; Diaquo-5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(III) Hexafluorophosphate; Diaquo-4,10-dimethyl-1,4,7,10-tetraazabicyclo[5.5.2]tetradecane Manganese(II) Hexafluorophosphate; Diaquo-5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(II) Tetrafluoroborate; Diaquo-4,10-dimethyl-1,4,7,10-tetraazabicyclo[5.5.2]tetradecane Manganese(II) Tetrafluoroborate; Dichloro-5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(III); Hexafluorophosphate; Dichloro-5,12-di-n-butyl-1,5,8,12-tetraaza-bicyclo[6.6.2]hexadecane Manganese(II); Dichloro-5,12-dibenzyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(II); Dichloro-5-n-butyl-12-methyl-1,5,8,12-tetraaza-bicyclo[6.6.2]hexadecane Manganese(II); Dichloro-5-n-octyl-12-methyl-1,5,8,12-tetraaza-bicyclo[6.6.2]hexadecane Manganese(II); Dichloro-5-n-butyl-12-methyl-1,5,8,12-tetraaza-bicyclo[6.6.2]hexadecane Manganese(II); Dichloro-5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Iron(II); Dichloro-4,10-dimethyl-1,4,7,10-tetraazabicyclo[5.5.2]tetradecane Iron(II); Dichloro-5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Copper(II); Dichloro-4,10-dimethyl-1,4,7,10-tetraazabicyclo[5.5.2]tetradecane Copper(II); Dichloro-5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Cobalt(II); Dichloro-4,10-dimethyl-1,4,7,10-tetraazabicyclo[5.5.2]tetradecane Cobalt(II); Dichloro-5,12-dimethyl-4-phenyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(II); Dichloro-4,10-dimethyl-3-phenyl-1,4,7,10-tetraazabicyclo[5.5.2]tetradecane Manganese(II); Dichloro-5,12-dimethyl-4,9-diphenyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(II); Dichloro-4,10-dimethyl-3,8-diphenyl-1,4,7,10-tetraazabicyclo[5.5.2]tetradecane Manganese(II); Dichloro-5,12-dimethyl-2,11-diphenyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(II); Dichloro-4,10-dimethyl-4,9-diphenyl-1,4,7,10-tetraazabicyclo[5.5.2]tetradecane Manganese(II); Dichloro-2,4,5,9,11,12-hexamethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(II); Dichloro-2,3,5,9,10,12-hexamethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(II); Dichloro-2,2,4,5,9,11,12-octamethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(II); Dichloro-2,2,4,5,9,11,11,12-octamethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(II); Dichloro-3,3,5,10,10,12-hexamethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(II); Dichloro-3,5,10,12-tetramethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(II); Dichloro-3-butyl-5,10,12-trimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(II); Dichloro-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Man-

ganese(II); Dichloro-1,4,7,10-tetraazabicyclo[5.5.2]tetradecane Manganese(II); Dichloro-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Iron(II); Dichloro-1,4,7,10-tetraazabicyclo[5.5.2]tetradecane Iron(II); Aquo-chloro-2-(2-hydroxyphenyl)-5,12-dimethyl-5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(II); Aquo-chloro-10-(2-hydroxybenzyl)-4,10-dimethyl-1,4,7,10-tetraazabicyclo[5.5.2]tetradecane Manganese(II); Chloro-2-(2-hydroxybenzyl)-5-methyl-5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(II); Chloro-10-(2-hydroxybenzyl)-4-methyl-1,4,7,10-tetraazabicyclo[5.5.2]tetradecane Manganese(II); Chloro-5-methyl-12-(2-picolyl)-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(II) Chloride; Chloro-4-methyl-10-(2-picolyl)-1,4,7,10-tetraazabicyclo[5.5.2]tetradecane Manganese(II) Chloride; Dichloro-5-(2-sulfato)dodecyl-12-methyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(III); Aquo-Chloro-5-(2-sulfato)dodecyl-12-methyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(II); Aquo-Chloro-5-(3-sulfonopropyl)-12-methyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(II); Dichloro-5-(Trimethylammoniopropyl)dodecyl-12-methyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(III) Chloride; Dichloro-5,12-dimethyl-1,4,7,10,13-pentaazabicyclo[8.5.2]heptadecane Manganese(II); Dichloro-14,20-dimethyl-1,10,14,20-tetraazatrieyclo[8.6.6]docosa-3(8),4,6-triene Manganese(II); Dichloro-4,11-dimethyl-1,4,7,11-tetraazabicyclo[6.5.2]pentadecane Manganese(II); Dichloro-5,12-dimethyl-1,5,8,12-tetraazabicyclo[7.6.2]heptadecane Manganese(II); Dichloro-5,13-dimethyl-1,5,9,13-tetraazabicyclo[7.7.2]heptadecane Manganese(II); Dichloro-3, 10-bis(butylcarboxy)-5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(II); Diaquo-3,10-dicarboxy-5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(II); Chloro-20-methyl-1,9,20,24,25-pentaaza-tetracyclo[7.7.7.1^{3,7}.1^{11,15}].pentacosa-3,5,7(24),11,13,15(25)-hexaene manganese(II) Hexafluorophosphate; Trifluoromethanesulfono-20-methyl-1,9,20,24,25-pentaaza-tetracyclo[7.7.7.1^{3,7}.1^{11,15}].pentacosa-3,5,7(24),11,13,15(25)-hexaene Manganese(II) Trifluoromethanesulfonate; Trifluoromethanesulfono-20-methyl-1,9,20,24,25-pentaaza-tetracyclo[7.7.7.1^{3,7}.1^{11,15}].pentacosa-3,5,7(24),11,13,15(25)-hexaene Iron(II) Trifluoromethanesulfonate; Chloro-5,12,17-trimethyl-1,5,8,12,17-pentaazabicyclo[6.6.5]nonadecane Manganese(II) Hexafluorophosphate; Chloro-4,10,15-trimethyl-1,4,7,10,15-pentaazabicyclo[5.5.5]heptadecane Manganese(II) Hexafluorophosphate; Chloro-5,12,17-trimethyl-1,5,8,12,17-pentaazabicyclo[6.6.5]nonadecane Manganese(II) Chloride; Chloro-4,10,15-trimethyl-1,4,7,10,15-pentaazabicyclo[5.5.5]heptadecane Manganese(II) Chloride; Dichloro-5,12-diethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecanemanganese; and any mixture thereof.

[0046] Other suitable transition metal bleach catalysts are described in U.S. 5,580,485, U.S. 4,430,243; U.S. 4,728,455; U.S. 5,246,621; U.S. 5,244,594; U.S. 5,284,944; U.S. 5,194,416; U.S. 5,246,612; U.S. 5,256,779; U.S. 5,280,117; U.S. 5,274,147; U.S. 5,153,161; U.S. 5,227,084; U.S. 5,114,606; U.S. 5,114,611, EP 549,271 A1; EP 544,490 A1; EP 549,272 A1; and EP 544,440 A2.

[0047] A suitable transition metal bleach catalyst is a manganese-based catalyst, for example disclosed in U.S. 5,576,282.

[0048] Suitable cobalt bleach catalysts are described, for example, in U.S. 5,597,936 and U.S. 5,595,967. Such cobalt catalysts are readily prepared by known procedures, such as taught for example in U.S. 5,597,936, and U.S. 5,595,967.

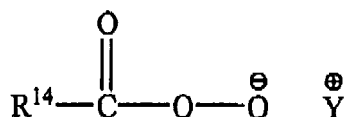
[0049] A suitable transition metal bleach catalyst is a transition metal complex of ligand such as bispidones described in WO 05/042532 A1.

[0050] The inventors have found that transition metal bleach catalysts provide robust cleaning profiles, especially under dilute wash conditions, and especially against beta-carotene, squalene and unsaturated triglyceride soils, and especially at low washing temperatures.

Pre-formed peracid

[0051] The laundry detergent composition may comprise a pre-formed peracid. The preperoxyacid or salt thereof is typically either a peroxycarboxylic acid or salt thereof, or a peroxysulphonic acid or salt thereof.

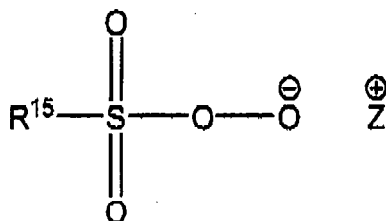
[0052] The pre-formed peroxyacid or salt thereof is preferably a peroxycarboxylic acid or salt thereof, typically having a chemical structure corresponding to the following chemical formula:



wherein: R¹⁴ is selected from alkyl, aralkyl, cycloalkyl, aryl or heterocyclic groups; the R¹⁴ group can be linear or branched, substituted or unsubstituted; and Y is any suitable counter-ion that achieves electric charge neutrality, preferably Y is selected from hydrogen, sodium or potassium. Preferably, R¹⁴ is a linear or branched, substituted or unsubstituted C₆₋₉ alkyl. Preferably, the peroxyacid or salt thereof is selected from peroxyhexanoic acid, peroxyheptanoic acid, peroxy-

octanoic acid, peroxy-nonanoic acid, peroxy-decanoic acid, any salt thereof, or any combination thereof. Preferably, the peroxyacid or salt thereof has a melting point in the range of from 30°C to 60°C.

[0053] The pre-formed peroxyacid or salt thereof can also be a peroxysulphonic acid or salt thereof, typically having a chemical structure corresponding to the following chemical formula:



wherein: R¹⁵ is selected from alkyl, aralkyl, cycloalkyl, aryl or heterocyclic groups; the R¹⁵ group can be linear or branched, substituted or unsubstituted; and Z is any suitable counter-ion that achieves electric charge neutrality, preferably Z is selected from hydrogen, sodium or potassium. Preferably R¹⁵ is a linear or branched, substituted or unsubstituted C₆₋₉ alkyl.

[0054] The pre-formed peroxyacid or salt thereof may be in an encapsulated, preferably molecularly encapsulated, form. Typically, the pre-formed peroxyacid molecules are individually separated from each other by any suitable molecular encapsulation means.

[0055] Preferably, the pre-formed peroxyacid is a guest molecule in a host-guest complex. Typically, the host molecule of the host-guest complex comprises, or is capable of forming (e.g. by their intermolecular configuration), a cavity into which the pre-formed peroxyacid molecule can be located. The host molecule is typically in the form of a relatively open structure which provides a cavity that may be occupied by a pre-formed peroxyacid molecule: thus forming the host-guest complex. The pre-formed peroxyacid molecule may become entrapped by one or more host molecules, for example by the formation of a clathrate compound, also typically known as inclusion compound, cage compound, molecular compound, intercalation compound or adduct.

[0056] The host molecule is typically capable of forming hydrogen bonds: such as intramolecular hydrogen bonds or intermolecular hydrogen bonds. Preferably, the host molecule is capable of forming intermolecular hydrogen bonds.

[0057] Suitable host molecules include: urea; cyclodextrins, particularly beta-cyclodextrins; thiourea; hydroquinone; perhydrotriphenylene; deoxycholic acid; triphenylcarbinol; calixarene; zeolites, particularly wide-pore zeolites; and any combination thereof. The host molecules are most preferably water-soluble; this is desirable so as to enable the effective release and dispersion of the pre-formed peroxyacid on introduction of the host-guest complex into an aqueous environment, such as a wash liquor. Preferably, the host molecule is urea or thiourea, especially preferably the host molecule is urea.

[0058] The host-guest complex is preferably at least partially, preferably essentially completely, coated by a coating ingredient; this is desirable so as to further improve the stability of the pre-formed peroxyacid. Typically, the coating ingredient is essentially incapable of forming hydrogen bonds; this helps ensure the optimal intermolecular configuration of the host molecules, especially when the host-guest complex is a clathrate compound, and further improves the stability of the pre-formed peroxyacid. Typically, the coating ingredient is chemically compatible with the host-guest complex and has a suitable release profile, especially an appropriate melting point range: the melting point range of the coating ingredient is preferably from 35°C to 60°C, more preferably from 40°C to 50°C, or from 46°C to 68°C. Suitable coating ingredients include paraffin waxes, semi-microcrystalline waxes (also typically known as intermediate-microcrystalline waxes), microcrystalline waxes and natural waxes. Preferred paraffin waxes include: Merck® 7150 and Merck® 7151 supplied by E. Merck of Darmstadt, Germany; Boler® 1397, Boler® 1538 and Boler® 1092 supplied by Boler of Wayne, Pa.; Ross® fully refined paraffin wax 115/120 supplied by Frank D. Ross Co., Inc of Jersey City, N.J.; Tholler® 1397 and Tholler® 1538 supplied by Tholler of Wayne, Pa.; Paramelt® 4608 supplied by Terhell Paraffin of Hamburg, Germany and Paraffin® R7214 supplied by Moore & Munger of Shelton, Conn. Preferred paraffin waxes typically have a melting point in the range of from 46°C to 68°C, and they typically have a number average molecular weight in the range of from 350Da to 420Da. Also suitable are: natural waxes, such as natural bayberry wax, having a melting point in the range of from 42°C to 48°C supplied by Frank D. Ross Co., Inc.; synthetic substitutes of natural waxes, such as synthetic spermaceti wax, having a melting point in the range of from 42°C to 50°C, supplied by Frank D. Ross Co.; Inc., synthetic beeswax (BD4) and glyceryl behenate (HRC) synthetic wax. Other suitable coating ingredients include fatty acids, especially hydrogenated fatty acids. However, most preferably the coating ingredient is a paraffin wax.

[0059] Typically, the host-guest complex is in an intimate mixture with a source of acid. Typically, the host-guest complex and the source of acid are in particulate form, preferably being in a co-particulate mixture with each other:

typically both are present in the same particle. Preferred sources of acid include: fatty acids, especially hydrogenated fatty acids, which may also be suitable coating ingredients and are described above; carboxylic acids, including mono-carboxylic acids, and poly-carboxylic acids such as di-carboxylic acids and tri-carboxylic acids. Preferably, the source of acid is a bi-carboxylic acid.

[0060] It may be preferred for the host-guest complex to be in an intimate mixture with a free radical scavenger. A suitable free radical scavenger is butylated hydroxytoluene.

[0061] Without wishing to be bound by theory, the inventors believe that the pre-formed peracid's has the ability to bleach even in the absence of an alkalinity source or hydrogen peroxide. The pre-formed peracid is not susceptible to the effects of catalase. This means that on a weight basis, the pre-formed peracid provides a good bleaching performance as one compacts the alkalinity/buffer systems and the wash liquor pH decreases.

Source of hydrogen peroxide

[0062] The composition preferably comprises a source of hydrogen peroxide, preferably from above 0wt% to 15wt%, preferably from 1wt%, or from 2wt%, or from 3wt%, or from 4wt%, or from 5wt%, and preferably to 12wt%, or preferably from 0wt% to 10wt% source of hydrogen peroxide. Preferably, the source of hydrogen peroxide is coated, preferred coatings include sulphate salts, silicate salts, carbonate salts, burkeite, borosilicate, and any mixture thereof including any double salt thereof. Preferably, the wash liquor comprises from above 0g/l to 0.5g/l hydrogen peroxide, preferably from 0.01 g/l, and preferably to 0.4g/l, or even to 0.3g/l, or even to 0.2g/l, or even to 0.1g/l. Preferably, the laundry detergent composition comprises a source of hydrogen peroxide in an amount such that during the method of the present invention from above 0g to 1.5g, or to 1.0g, or to 0.8g, or to 0.6g, or to 0.5g, or to 0.4g source of hydrogen peroxide per litre of water is contacted to said water when forming the wash liquor.

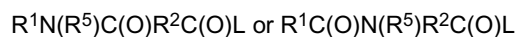
[0063] Typically, the source of hydrogen peroxide comprises from 10% to 100%, by weight of the source of hydrogen peroxide, of hydrogen peroxide.

[0064] Preferred sources of hydrogen peroxide include sodium perborate in, preferably in monohydrate or tetra-hydrate form or mixtures thereof, sodium percarbonate. Especially preferred is sodium percarbonate. The sodium percarbonate can be in the form of a coated percarbonate particle, the particle being a physically separate and discrete particle from the other particles of the laundry detergent composition, and especially from any bleach activator or the bleach ingredient. Alternatively, the percarbonate can be in the form of a co-particle that additionally comprises a bleach activator such as tetra-ethylene diamine (TAED) and the bleach ingredient. Highly preferred, when a co-particle form is used, a bleach activator at least partially, preferably completely, encloses the source of hydrogen peroxide.

Bleach activator

[0065] Preferably, the composition comprises a bleach activator. Suitable bleach activators are compounds which when used in conjunction with a hydrogen peroxide source leads to the in situ production of the peracid corresponding to the bleach activator. Various non limiting examples of bleach activators are disclosed in U.S. Patent 4,915,854, issued April 10, 1990 to Mao et al, and U.S. Patent 4,412,934. The nonanoyloxybenzene sulfonate (NOBS) and tetraacetylenediamine (TAED) activators are typical, and mixtures thereof can also be used. See also U.S. 4,634,551 for other typical bleaches and activators useful herein. Another suitable bleach activator is decanoyloxybenzenecarboxylic acid (DOBA).

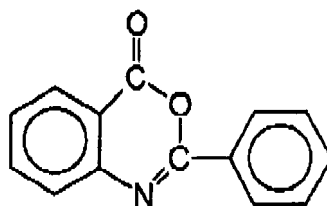
[0066] Highly preferred amido-derived bleach activators are those of the formulae:



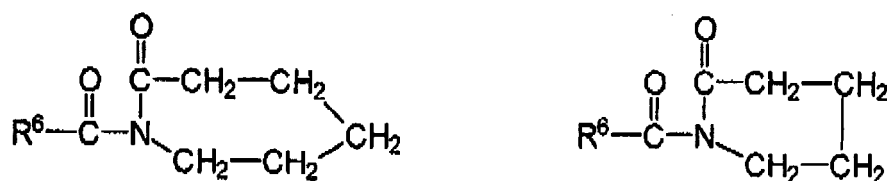
wherein as used for these compounds R^1 is an alkyl group containing from about 6 to about 12 carbon atoms, R^2 is an alkylene containing from 1 to about 6 carbon atoms, R^5 is H or alkyl, aryl, or alkaryl containing from about 1 to about 10 carbon atoms, and L is any suitable leaving group. A leaving group is any group that is displaced from the bleach activator as a consequence of the nucleophilic attack on the bleach activator by the hydroperoxide anion. A preferred leaving group is oxybenzenesulfonate.

[0067] Preferred examples of bleach activators of the above formulae include (6-octanamidocaproyl)oxybenzenesulfonate, (6-nonanamidocaproyl)oxybenzenesulfonate, (6-decanamidocaproyl)oxybenzenesulfonate, and mixtures thereof as described in U.S. Patent 4,634,551, incorporated herein by reference.

[0068] Another class of bleach activators comprises the benzoxazin-type activators disclosed by Hodge et al in U.S. Patent 4,966,723, issued October 30, 1990, incorporated herein by reference. A highly preferred activator of the benzoxazin-type is:



[0069] Still another class of preferred bleach activators includes the acyl lactam activators, especially acyl caprolactams and acyl valerolactams of the formulae:



wherein as used for these compounds R^6 is H or an alkyl, aryl, alkoxyaryl, or alkaryl group containing from 1 to about 12 carbon atoms. Highly preferred lactam activators include benzoyl caprolactam, octanoyl caprolactam, 3,5,5-trimethylhexanoyl caprolactam, nonanoyl caprolactam, decanoyl caprolactam, undecenoyl caprolactam, benzoyl valerolactam, octanoyl valerolactam, decanoyl valerolactam, undecenoyl valerolactam, nonanoyl valerolactam, 3,5,5-trimethylhexanoyl valerolactam and mixtures thereof. See also U.S. Patent 4,545,784, issued to Sanderson, October 8, 1985, incorporated herein by reference, which discloses acyl caprolactams, including benzoyl caprolactam, adsorbed into sodium perborate. Highly preferred bleach activators are nonanoyloxybenzene sulfonate (NOBS) and/or tetraacetythylenediamine (TAED).

[0070] It is highly preferred for a large amount of bleach activator relative to the source of hydrogen peroxide to be present in the laundry detergent composition. Preferably, the weight ratio of bleach activator to source of hydrogen peroxide present in the laundry detergent composition is at least 0.5:1, at least 0.6:1, at least 0.7:1, 0.8:1, preferably at least 0.9:1, or 1.0:1.0, or even 1.2:1 or higher.

Layered particle

[0071] In a highly preferred embodiment of the present invention, the laundry detergent composition comprises a layered particle. The layered particle comprises a core and a layer. The core comprises a source of hydrogen peroxide. The layer comprises a binder and a bleach activator. The weight ratio of said source of hydrogen peroxide to said bleach activator present in the layered particle is preferably from about 5:1 to about 1.1:1, or from about 4:1 to about 1.5:1, or about 2:1.

[0072] Preferably, the layered particle may have an average diameter of from about 600 μm to 2000 μm , or from about 800 μm to about 1000 μm . In one aspect, the layer may have a thickness of from about 25 μm to about 150 μm , or from about 40 μm to about 100 μm .

[0073] Preferably, the binder may comprise, based on total layered particle weight, from about 2% to about 20%, or from about 4% to about 15%, or about 6% to about 10%, or from about 7% to about 8% of said layered particle. The binder may comprise, based on total layered particle weight, from about 0.001 % to about 5%, or from about 0.5% to about 3%, or about 1% to about 2% water. In one aspect, the binder may be substantially free of water. In one aspect, the binder may be capable of absorbing from about 0.1% to about 20%, or from about 1% to about 15%, or from about 2% to about 10% water by weight of said binder over a relative humidity of 80% at 32°C. In one aspect, the binder may have a viscosity of from about 200 to about 20,000, or from about 500 to about 7,000, or from about 1,000 to about 2,000 centipoise at a shear rate of 25 sec^{-1} at 25°C.

[0074] The binder may comprise, based on total binder weight, from about 40% to 100%, or about 50% to about 99% of a surfactant material selected from the group consisting of anionic surfactant, nonionic surfactant, and combinations thereof, more preferably alcohol ethoxylate and linear alkylbenzene sulfonate. In one aspect, the binder may comprise,

based on total binder weight, from about 60% to about 100%, or about 70% to about 90%, of a non-surfactant material comprising a hydrocarbon material selected from the group consisting of fats, triglycerides, lipids, fatty acids, soft paraffin wax, and combinations thereof

[0075] The binder may have a pH of from about 3 to about 9, or from about 5 to about 8, or about 7, as measured as a 10% solution in water. In one aspect, the binder may comprise a solvent.

[0076] The layered particle may comprise a dusting powder that may comprise a material selected from the group consisting of silicas; zeolites; amorphous aluminosilicates; clays; starches; celluloses; water soluble salts, such as an inorganic salt selected from the group consisting of, sodium chloride, sodium sulphate, magnesium sulphate, and salts and mixtures thereof; polysaccharides including sugars; and combinations thereof

[0077] The layer may comprise an additive selected from the group consisting of acidic materials, moisture sinks; gelling agents; antioxidants; organic catalysts and combinations thereof.

[0078] In one aspect, the additive may comprise an acidic material having a pKa of from about 3 to about 7, or about 5. In one aspect, the acidic material may be ascorbic acid.

[0079] In one aspect, the additive may comprise a moisture sink that may be selected from the group consisting of crosslinked polyacrylates; sodium salts of maleic/acrylic copolymers; magnesium sulfate; and combinations thereof.

[0080] In one aspect, the additive may comprise a gelling agent that may be selected from the group consisting of a cellulose including methylcellulose and CMC; alginate and derivatives thereof; starches; polyvinyl alcohols; polyethylene oxide; polyvinylpyrrolidone; polysaccharides including chitosan and/or natural gums including carrageenan, xanthan gum, guar gum, locust bean gum, and combinations thereof; polyacrylates including cross-linked polyacrylates; alcohol ethoxylates; lignosulfonates; surfactants and mixtures thereof; powdered anionic surfactants; and combinations thereof.

[0081] In one aspect, the additive may comprise an antioxidant that may be selected from the group consisting of phenolic antioxidants; amine antioxidants; alkylated phenols; hindered phenolic compounds; benzofuran or benzopyran; alpha-tocopherol, beta-tocopherol, gamma-tocopherol, delta-tocopherol, and derivatives thereof; 6-hydroxy-2,5,7,8-tetra-methylchroman-2-carboxylic acid; ascorbic acid and its salts; butylated hydroxy benzoic acids and their salts; gallic acid and its alkyl esters; uric acid and its salts and alkyl esters; sorbic acid and its salts; amines; sulfhydryl compounds; dihydroxy fumaric acid and its salts; and combinations thereof, 2,6-di-tert-butylphenol; 2,6-di-tert-butyl-4-methylphenol; mixtures of 2 and 3-tert-butyl-4-methoxyphenol; propyl gallate; tert-butylhydroquinone; benzoic acid derivatives such as methoxy benzoic acid; methylbenzoic acid; dichloro benzoic acid; dimethyl benzoic acid; 5-hydroxy-2,2,4,6,7-pentamethyl-2,3-dihydro-1-benzofuran-3-one; 5-hydroxy-3-methylene-2,2,4,6, 7-pentamethyl-2,3-dihydro-benzofuran; 5-benzoyloxy-3-hydroxymethyl-2,2,4,6,7-pentamethyl-2,3-dihydro-1-benzofuran; 3-hydroxymethyl-5-methoxy-2,2,4,6,7-pentamethyl-2,3-dihydro-1-benzofuran; ascorbic acid; 1,2-dihydro-6-ethoxy-2,2,4-trimethylchinolin, and combinations thereof; 2,6-di-tert-butyl hydroxy toluene; alpha-tocopherol; hydroquinone, 2,2,4-trimethyl-1,2-dihydroquinoline; 2,6-di-tert-butyl hydroquinone; 2-tert-butyl hydroquinone; tert-butyl-hydroxy anisole; lignosulphonic acid and salts thereof; benzoic acid and derivatives thereof; trimethoxy benzoic acid; toluic acid; catechol; t-butyl catechol; benzylamine; amine alcohols; 1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl) butane; N-propyl-gallate or mixtures thereof; or di-tert-butyl hydroxy toluene.

[0082] In one aspect, the additive may comprise an organic catalyst that may be selected from the group consisting of iminium cations and polyions; iminium zwitterions; modified amines; modified amine oxides; N-sulphonyl imines; N-phosphonyl imines; N-acyl imines; thiadiazole dioxides; perfluoroimines; cyclic sugar ketones; and combinations thereof; or an organic catalyst selected from the group consisting of 2-[3-[(2-hexyldodecyl)oxy]-2-(sulfooxy)propyl]-3,4-dihydroisoquinolinium, inner salt; 3,4-dihydro-2-[3-[(2-pentylundecyl)oxy]-2-(sulfooxy)propyl]isoquinolinium, inner salt; 2-[3-[(2-butyldecyl)oxy]-2-(sulfooxy)propyl]-3,4-dihydroisoquinolinium, inner salt; 3,4-dihydro-2-[3-(octadecyloxy)-2-(sulfooxy)propyl]isoquinolinium, inner salt; 2-[3-(hexadecyloxy)-2-(sulfooxy)propyl]-3,4-dihydroisoquinolinium, inner salt; 3,4-dihydro-2-[2-(sulfooxy)-3-(tetradecyloxy)propyl]isoquinolinium, inner salt; 2-[3-(dodecyloxy)-2-(sulfooxy)propyl]-3,4-dihydroisoquinolinium, inner salt; 2-[3-[(3-hexyldecyl)oxy]-2-(sulfooxy)propyl]-3,4-dihydroisoquinolinium, inner salt; 3,4-dihydro-2-[3-[(2-pentylnonyl)oxy]-2-(sulfooxy)propyl]isoquinolinium, inner salt; 3,4-dihydro-2-[3-[(2-propylheptyl)oxy]-2-(sulfooxy)propyl]isoquinolinium, inner salt; 2-[3-[(2-butylloctyl)oxy]-2-(sulfooxy)propyl]-3,4-dihydroisoquinolinium, inner salt; 2-[3-(decyloxy)-2-(sulfooxy)propyl]-3,4-dihydroisoquinolinium, inner salt; 3,4-dihydro-2-[3-(octyloxy)-2-(sulfooxy)propyl]isoquinolinium, inner salt; 2-[3-[(2-ethylhexyl)oxy]-2-(sulfooxy)propyl]-3,4-dihydroisoquinolinium, inner salt or mixtures thereof; or 2-[3-[(2-butylloctyl)oxy]-2-(sulfooxy)propyl]-3,4-dihydroisoquinolinium, inner salt.

[0083] In one aspect, the layered particle may be substantially free of fatty acids, fatty acid polyol esters, polyglycols, and fatty alcohol oxalkylates.

Chelant

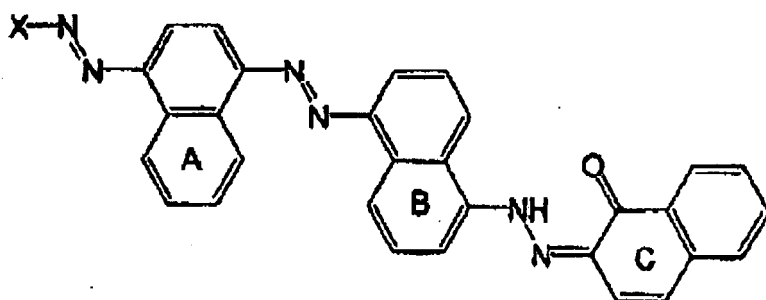
[0084] The composition may comprise a chelant. Suitable chelants include diethylene triamine pentaacetate, diethylene triamine penta(methyl phosphonic acid), ethylene diamine-N,N'-disuccinic acid, ethylene diamine tetraacetate, ethylene diamine tetra(methylene phosphonic acid) and hydroxyethane di(methylene phosphonic acid). A preferred chelant is

ethylene diamine-N'N'-disuccinic acid (EDDS) and/or hydroxyethane diphosphonic acid (HEDP). The laundry detergent composition preferably comprises ethylene diamine-N'N'-disuccinic acid or salt thereof. Preferably the ethylene diamine-N'N'-disuccinic acid is in S'S' enantiomeric form. Preferably the composition comprises 4,5-dihydroxy-m-benzenedisulfonic acid disodium salt.

Fabric hueing agent

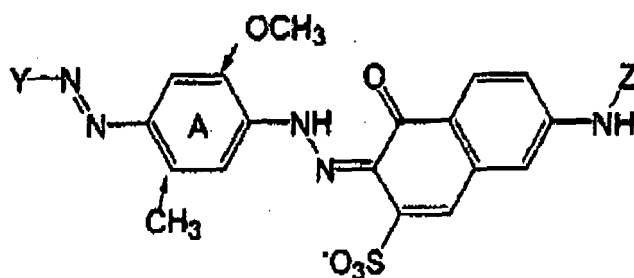
[0085] Suitable fabric hueing agents include dyes, dye-clay conjugates, and pigments that preferably satisfy the requirements of Test Method 1, described herein below. Suitable dyes include small molecule dyes and polymeric dyes. Suitable small molecule dyes include small molecule dyes selected from the group consisting of dyes falling into the Colour Index (C.I.) classifications of Direct Blue, Direct Red, Direct Violet, Acid Blue, Acid Red, Acid Violet, Basic Blue, Basic Violet and Basic Red, or mixtures thereof, for example:

(1) Tris-azo direct blue dyes of the formula



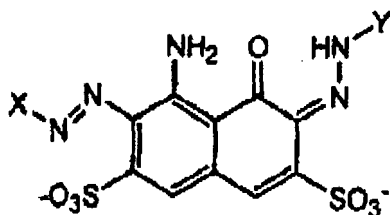
where at least two of the A, B and C naphthyl rings are substituted by a sulfonate group, the C ring may be substituted at the 5 position by an NH_2 or NHPh group, X is a benzyl or naphthyl ring substituted with up to 2 sulfonate groups and may be substituted at the 2 position with an OH group and may also be substituted with an NH_2 or NHPh group.

(2) bis-azo Direct violet dyes of the formula:



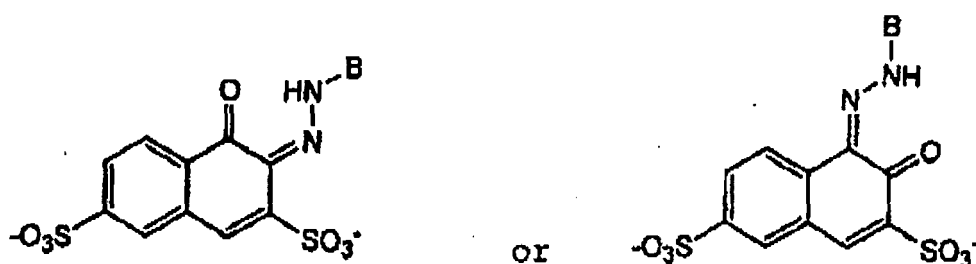
where Z is H or phenyl, the A ring is preferably substituted by a methyl and methoxy group at the positions indicated by arrows, the A ring may also be a naphthyl ring, the Y group is a benzyl or naphthyl ring, which is substituted by sulfate group and may be mono or disubstituted by methyl groups.

(3) Blue or red acid dyes of the formula



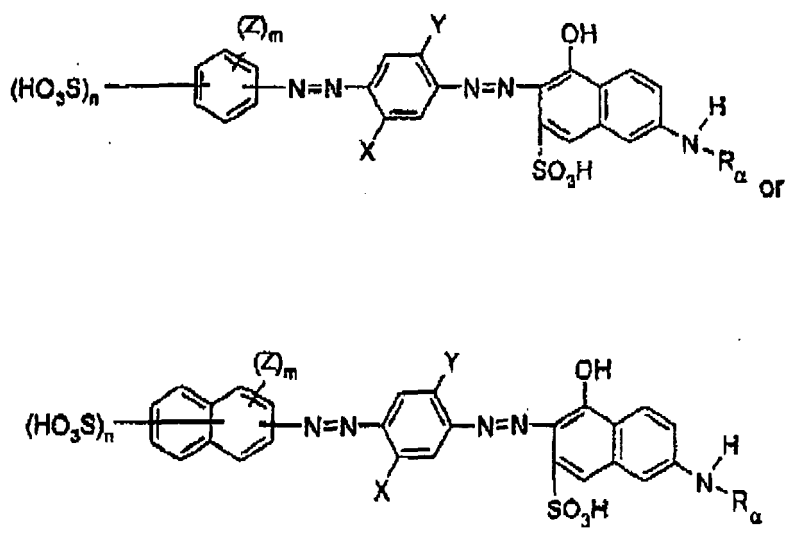
where at least one of X and Y must be an aromatic group. In one aspect, both the aromatic groups may be a substituted benzyl or naphthyl group, which may be substituted with non water-solubilising groups such as alkyl or alkyloxy or aryloxy groups, X and Y may not be substituted with water solubilising groups such as sulfonates or carboxylates. In another aspect, X is a nitro substituted benzyl group and Y is a benzyl group

(4) Red acid dyes of the structure



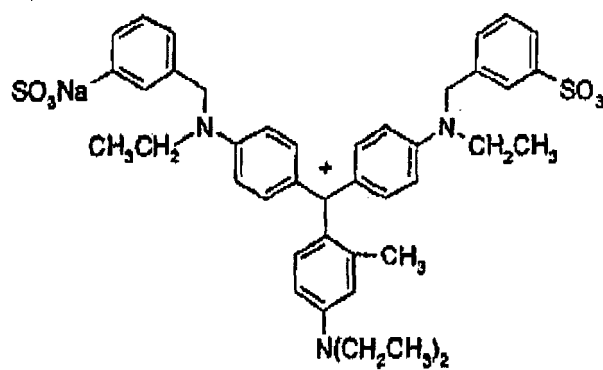
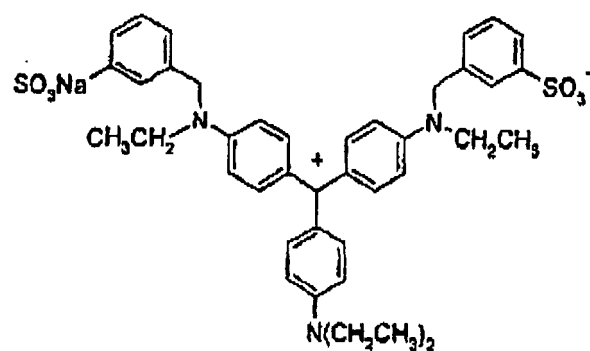
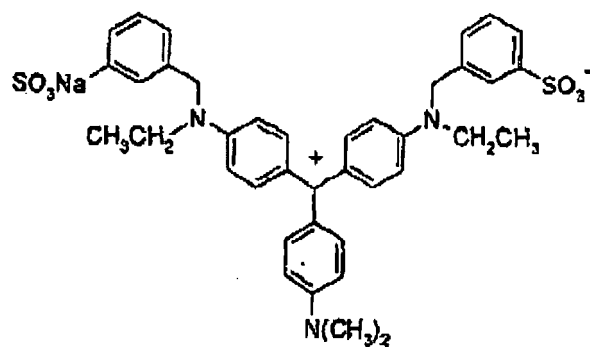
where B is a naphthyl or benzyl group that may be substituted with non water solubilising groups such as alkyl or alkyloxy or aryloxy groups, B may not be substituted with water solubilising groups such as sulfonates or carboxylates.

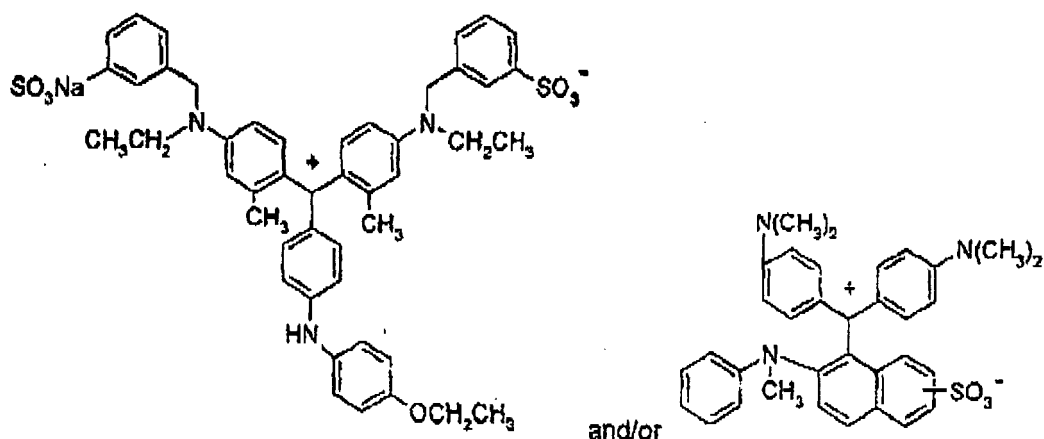
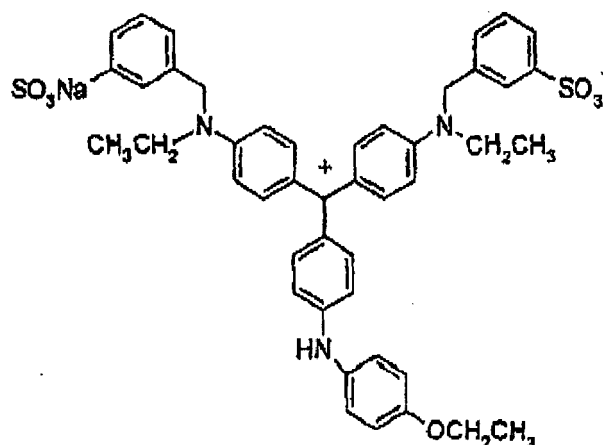
(5) Dis-azo dyes of the structure



wherein X and Y, independently of one another, are each hydrogen, C₁-C₄ alkyl or C₁-C₄-alkoxy, R_α is hydrogen or aryl, Z is C₁-C₄ alkyl; C₁-C₄-alkoxy; halogen; hydroxyl or carboxyl, n is 1 or 2 and m is 0, 1 or 2, as well as corresponding salts thereof and mixtures thereof

(6) Triphenylmethane dyes of the following structures





and mixtures thereof. In another aspect, suitable small molecule dyes include small molecule dyes selected from the group consisting of Colour Index (Society of Dyers and Colourists, Bradford, UK) numbers Direct Violet 9, Direct Violet 35, Direct Violet 48, Direct Violet 51, Direct Violet 66, Direct Blue 1, Direct Blue 71, Direct Blue 80, Direct Blue 279, Acid Red 17, Acid Red 73, Acid Red 88, Acid Red 150, Acid Violet 15, Acid Violet 17, Acid Violet 24, Acid Violet 43, Acid Red 52, Acid Violet 49, Acid Blue 15, Acid Blue 17, Acid Blue 25, Acid Blue 29, Acid Blue 40, Acid Blue 45, Acid Blue 75, Acid Blue 80, Acid Blue 83, Acid Blue 90 and Acid Blue 113, Acid Black 1, Basic Violet 1, Basic Violet 3, Basic Violet 4, Basic Violet 10, Basic Violet 35, Basic Blue 3, Basic Blue 16, Basic Blue 22, Basic Blue 47, Basic Blue 66, Basic Blue 75, Basic Blue 159 and mixtures thereof. In another aspect, suitable small molecule dyes include small molecule dyes selected from the group consisting of Colour Index (Society of Dyers and Colourists, Bradford, UK) numbers Acid Violet 17, Acid Violet 43, Acid Red 52, Acid Red 73, Acid Red 88, Acid Red 150, Acid Blue 25, Acid Blue 29, Acid Blue 45, Acid Blue 113, Acid Black 1, Direct Blue 1, Direct Blue 71, Direct Violet 51 and mixtures thereof. In another aspect, suitable small molecule dyes include small molecule dyes selected from the group consisting of Colour Index (Society of Dyers and Colourists, Bradford, UK) numbers Acid Violet 17, Direct Blue 71, Direct Violet 51, Direct Blue 1, Acid Red 88, Acid Red 150, Acid Blue 29, Acid Blue 113 or mixtures thereof.

[0086] Suitable polymeric dyes include polymeric dyes selected from the group consisting of polymers containing conjugated chromogens (dye-polymer conjugates) and polymers with chromogens co-polymerized into the backbone of the polymer and mixtures thereof.

[0087] In another aspect, suitable polymeric dyes include polymeric dyes selected from the group consisting of fabric-substantive colorants sold under the name of Liquitint® (Milliken, Spartanburg, South Carolina, USA), dye-polymer conjugates formed from at least one reactive dye and a polymer selected from the group consisting of polymers comprising a moiety selected from the group consisting of a hydroxyl moiety, a primary amine moiety, a secondary amine moiety, a thiol moiety and mixtures thereof. In still another aspect, suitable polymeric dyes include polymeric dyes selected from the group consisting of Liquitint® (Milliken, Spartanburg, South Carolina, USA) Violet CT, carboxymethyl cellulose (CMC)

conjugated with a reactive blue, reactive violet or reactive red dye such as CMC conjugated with C.I. Reactive Blue 19, sold by Megazyme, Wicklow, Ireland under the product name AZO-CM-CELLULOSE, product code S-ACMC, alkoxylated triphenyl-methane polymeric colourants, alkoxylated thiophene polymeric colourants, and mixtures thereof.

[0088] Suitable dye clay conjugates include dye clay conjugates selected from the group comprising at least one cationic/basic dye and a smectite clay, and mixtures thereof. In another aspect, suitable dye clay conjugates include dye clay conjugates selected from the group consisting of one cationic/basic dye selected from the group consisting of C.I. Basic Yellow 1 through 108, C.I. Basic Orange 1 through 69, C.I. Basic Red 1 through 118, C.I. Basic Violet 1 through 51, C.I. Basic Blue 1 through 164, C.I. Basic Green 1 through 14, C.I. Basic Brown 1 through 23, C.I. Basic Black 1 through 11, and a clay selected from the group consisting of Montmorillonite clay, Hectorite clay, Saponite clay and mixtures thereof. In still another aspect, suitable dye clay conjugates include dye clay conjugates selected from the group consisting of: Montmorillonite Basic Blue B7 C.I. 42595 conjugate, Montmorillonite Basic Blue B9 C.I. 52015 conjugate, Montmorillonite Basic Violet V3 C.I. 42555 conjugate, Montmorillonite Basic Green G1 C.I. 42040 conjugate, Montmorillonite Basic Red R1 C.I. 45160 conjugate, Montmorillonite C.I. Basic Black 2 conjugate, Hectorite Basic Blue B7 C.I. 42595 conjugate, Hectorite Basic Blue B9 C.I. 52015 conjugate, Hectorite Basic Violet V3 C.I. 42555 conjugate, Hectorite Basic Green G1 C.I. 42040 conjugate, Hectorite Basic Red R1 C.I. 45160 conjugate, Hectorite C.I. Basic Black 2 conjugate, Saponite Basic Blue B7 C.I. 42595 conjugate, Saponite Basic Blue B9 C.I. 52015 conjugate, Saponite Basic Violet V3 C.I. 42555 conjugate, Saponite Basic Green G1 C.I. 42040 conjugate, Saponite Basic Red R1 C.I. 45160 conjugate, Saponite C.I. Basic Black 2 conjugate and mixtures thereof.

[0089] Suitable pigments include pigments selected from the group consisting of flavanthrone, indanthrone, chlorinated indanthrone containing from 1 to 4 chlorine atoms, pyranthrone, dichloropyranthrone, monobromodichloropyranthrone, dibromodichloropyranthrone, tetrabromopyranthrone, perylene-3,4,9,10-tetracarboxylic acid diimide, wherein the imide groups may be unsubstituted or substituted by C1-C3 -alkyl or a phenyl or heterocyclic radical, and wherein the phenyl and heterocyclic radicals may additionally carry substituents which do not confer solubility in water, anthrapyrimidine-carboxylic acid amides, violanthrone, isoviolanthrone, dioxazine pigments, copper phthalocyanine which may contain up to 2 chlorine atoms per molecule, polychloro-copper phthalocyanine or polybromochloro-copper phthalocyanine containing up to 14 bromine atoms per molecule and mixtures thereof.

In another aspect, suitable pigments include pigments selected from the group consisting of Ultramarine Blue (C.I. Pigment Blue 29), Ultramarine Violet (C.I. Pigment Violet 15) and mixtures thereof.

[0090] The aforementioned fabric hueing agents can be used in combination (any mixture of fabric hueing agents can be used). Suitable fabric hueing agents can be purchased from Aldrich, Milwaukee, Wisconsin, USA; Ciba Specialty Chemicals, Basel, Switzerland; BASF, Ludwigshafen, Germany; Dayglo Color Corporation, Mumbai, India; Organic Dyestuffs Corp., East Providence, Rhode Island, USA; Dystar, Frankfurt, Germany; Lanxess, Leverkusen, Germany; Megazyme, Wicklow, Ireland; Clariant, Muttenz, Switzerland; Avecia, Manchester, UK and/or made in accordance with the examples contained herein.

[0091] Suitable hueing agents are described in more detail in US 7,208,459 B2.

TEST METHOD 1

[0092] A protocol to define whether a dye or pigment material is a fabric hueing agent for the purpose of the invention is given here:

- 1.) Fill two tergotometer pots with 800ml of Newcastle upon Tyne, UK, City Water (~12 grains per US gallon total hardness, supplied by Northumbrian Water, Pity Me, Durham, Co. Durham, UK).
- 2) Insert pots into tergotometer, with water temperature controlled at 30°C and agitation set at 40rpm for the duration of the experiment.
- 3) Add 4.8g of IEC-B detergent (IEC 60456 Washing Machine Reference Base Detergent Type B), supplied by wfk, Bruggen-Bracht, Germany, to each pot.
- 4) After two minutes, add 2.0mg active colorant to the first pot.
- 5) After one minute, add 50g of flat cotton vest (supplied by Warwick Equest, Consett, County Durham, UK), cut into 5cm x 5cm swatches, to each pot.
- 6) After 10 minutes, drain the pots and re-fill with cold Water (16°C) having a water hardness of 14.4 English Clark Degrees Hardness with a 3:1 Calcium to Magnesium molar ratio.
- 7) After 2 minutes rinsing, remove fabrics.
- 8) Repeat steps 3-7 for a further three cycles using the same treatments.
- 9) Collect and line dry the fabrics indoors for 12 hours.
- 10) Analyse the swatches using a Hunter Miniscan spectrometer fitted with D65 illuminant and UVA cutting filter, to obtain Hunter a (red-green axis) and Hunter b (yellow-blue axis) values.
- 11) Average the Hunter a and Hunter b values for each set of fabrics. If the fabrics treated with colorant under

assessment show an average difference in hue of greater than 0.2 units on either the a axis or b axis, it is deemed to be a fabric hueing agent for the purpose of the invention.

Enzyme

[0093] Extremely highly preferably, the laundry detergent composition comprises enzyme. Suitable enzymes include:

1. Enzymes from E.C. 1.1.3.x (oxidoreductases acting on CH-OH as donor and with oxygen as acceptor). Examples of suitable oxidoreductases categorized as E.C. 1.1.3.x are glucose oxidase, aryl-alcohol oxidase and galactose oxidase. A suitable hexose oxidase is OxyCo® 1500 (Danisco).

2. Enzymes from E.C. 1.11.x.x (oxidoreductases acting on peroxide as acceptor). An example of a suitable oxidoreductase acting on peroxide as acceptor is Guardzyme® (Novozymes).

3. Enzymes from E.C. 2.3.x.x (acyltransferases).

4. Enzymes from E.C. 2.4.x.x (glycosyl transferases).

5. Enzymes from E.C. 3.1.1.1 (carboxylesterase).

6. Enzymes from E.C. 3.1.1.3 (triacylglycerol lipase). Lipases have E.C. classification 3.1.1.3, as defined by EC classification, IUPAC-IUBMB. Suitable lipases include both wild-types and genetically modified variants thereof possessing at least about 90%, at least about 95%, at least about 98%, or at least about 99%, or 100% identity with said lipase. In one aspect, the lipase is a variant of the wild-type lipase from *Thermomyces lanuginosus* comprising the T231R and N233R mutations. The wild-type sequence is the 269 amino acids (amino acids 23 - 291) of the Swissprot accession number Swiss-Prot 059952 (derived from *Thermomyces lanuginosus* (*Humicola lanuginosa*)). Suitable commercially available lipases include Lipolase®, Lipolase Ultra®, Lipex® and Lipolex®, all available from Novozymes A/S.

7. Enzymes from E.C. 3.1.1.20 (tannase). Suitable tannases are disclosed in WO 06/002955A2.

8. Enzymes from E.C. 3.1.1.42 (chlorogenate hydrolase).

9. Enzymes from E.C. 3.1.1.73 (feruloyl esterase). Suitable ferulic acid esterases are derived from *Aspergillus awamori*, *Aspergillus tubingensis*, *Aspergillus niger*, *Talaromyces stipatus*, *Piromyces equi*, *cellvibrio japonicus*, *Talaromyces stipatus* and *Clostridium Japonicus*. Further suitable ferulic acid esterases are disclosed in *Acta Biochimica et Biophysica Sinica*, 2007, 39(11):811- 828, which is incorporated herein by reference.

10. Enzymes from E.C. 3.1.1.74 (cutinase). In one aspect, the enzyme may comprise a cutinase as defined by E.C. Class 3.1.1.73. The enzyme may have at least about 90% or about 95%, or about 98% identity with a wild-type from one of *Fusarium solani*, *Pseudomonas Mendocina* or *Humicola Insolens*.

11. Enzymes from E.C. 3.2.1.1 (α -amylase). Alpha amylases belong to E.C. Class 3.2.1.1. Suitable alpha-amylases include those of bacterial or fungal origin. Chemically or genetically modified mutants (variants) are included. A preferred alkaline alpha-amylase is derived from a strain of *Bacillus*, such as *Bacillus licheniformis*, *Bacillus amyloliquefaciens*, *Bacillus stearothermophilus*, *Bacillus subtilis*, or other *Bacillus* sp., such as *Bacillus* sp. NCIB 12289, NCIB 12512, NCIB 12513, DSM 9375 (USP 7,153,818) DSM 12368, DSMZ no. 12649, KSM AP1378 (WO 97/00324), KSM K36 or KSM K38 (EP 1,022,334). Preferred amylases include:

(a) the variants described in WO 94/02597, WO 94/18314, WO96/23874 and WO 97/43424, especially the variants with substitutions in one or more of the following positions versus the enzyme listed as SEQ ID No. 2 in WO 96/23874: 15, 23, 105, 106, 124, 128, 133, 154, 156, 181, 188, 190, 197, 202, 208, 209, 243, 264, 304, 305, 391, 408, and 444;

(b) the variants described in USP 5,856,164 and WO99/23211 WO 96/23873, WO00/60060 and WO 06/002643, especially the variants with one or more substitutions in the following positions versus the AA560 enzyme listed as SEQ ID No. 12 in WO 06/002643: 26, 30, 33, 82, 37, 106, 118, 128, 133, 149, 150, 160, 178, 182, 186, 193, 203, 214, 231, 256, 257, 258, 269, 270, 272, 283, 295, 296, 298, 299, 303, 304, 305, 311, 314, 315, 318, 319, 339, 345, 361, 378, 383, 419, 421, 437, 441, 444, 445, 446, 447, 450, 461, 471, 482, 484, preferably that also contain the deletions of D183* and G184*; and

(c) variants exhibiting at least 90% identity with SEQ ID No. 4 in WO06/002643, the wild-type enzyme from *Bacillus* SP722, especially variants with deletions in the 183 and 184 positions and variants described in WO 00/60060, which is incorporated herein by reference. Suitable commercially available alpha-amylases are DU-RAMYL®, LIQUEZYME®, TERMAMYL®, TERMAMYL ULTRA®, NATALASE®, SUPRAMYL®, STA1NZYME®, STAINZYME PLUS®, FUNGAMYL® and BAN® (Novozymes A/S), BIOAMYLASE - D(G), BIOAMYLASE® L (Biocon India Ltd.), KEMZYM® AT 9000 (Biozym Ges. m.b.H, Austria), RAPIDASE®, PURASTAR®, OPTISIZE HT PLUS® and PURASTAR OXAM® (Genencor International Inc.) and KAM® (KAO, Japan). In one aspect, preferred amylases are NATALASE®, STAINZYME® and STAINZYME PLUS®.

12. Enzymes from E.C. 3.2.1.2 (β -amylase).

13. Enzymes from E.C. 3.2.1.4 (cellulase), E.C. 3.2.1.21 (β -glucosidase) and E.C. 3.2.1.91 (cellulose 1,4- β -cellobiosidase). Suitable cellulases include cellulases from the genera *Bacillus*, *Pseudomonas*, *Humicola*, *Fusarium*, *Thielavia*, *Acremonium*, e.g. the fungal cellulases produced from *Humicola insolens*, *Myceliophthora thermophila*, *Fusarium oxysporum* disclosed in US 4,435,307, US 5,648,263, US 5,691,178, US 5,776,757 and WO 89/09259. Other suitable cellulases are the alkaline or neutral cellulases having colour care benefits. Examples of such cellulases are cellulases described in EP 0 495 257, EP 0 531 372, WO 96/1 1262, WO 96/29397, WO 98/08940. Other examples are cellulase variants such as those described in WO 94/07998, EP 0 531 315, US 5,457,046, US 5,686,593, US 5,763,254, WO 95/24471, WO 98/12307 and WO 99/01544, and WO 01/062903. Commercially available cellulases include Celluclean®, Celluzyme®, Renozyme® and Garezyme®; (Novozymes A/S), Clazina®; and Puradax HA®; (Genencor International Inc.), and KAC® 500; (Kao Corporation) and those sold under the Biotouch® and Ecoston® brand names (AB Enzymes).

Particularly suitable cellulases are variants of the Family 44 cellulase showing xyloglucanase activity disclosed in WO 2001/062903 (Novozymes).

14. Enzymes from E.C. 3.2.1.20 (α -glucosidase).

15. Enzymes from E.C. 3.2.1.25 (β -mannosidase) and E.C. 3.2.1.78 (mannan endo-1,4- β -mannosidase). Suitable mannan endo-1,4- β -mannosidases are described in WO 99/09126, WO 99/64573 and WO 99/09128. Preferred mannanases are sold under the tradenames Mannaway® (Novozymes A/S) and Purabritc® (Genencor International).

16. Enzymes from E.C. 3.2.1.151 (xyloglucan-specific endo- β -1,4-glucanase).

17. Enzymes from E.C. 3.2.1.155 (xyloglucan-specific exo- β -1,4-glucanase).

18. Enzymes from E.C. 3.4.x.x (peptidases). Suitable proteases include those of animal, vegetable or microbial origin. Microbial origin is preferred. Chemically or genetically modified mutants are included. The protease may be a serine protease, preferably an alkaline microbial protease or a trypsin-like protease. Examples of neutral or alkaline proteases include:

(a) subtilisins (EC 3.4.21.62), especially those derived from *Bacillus*, such as *Bacillus lentus*, *B. alkalophilus*, *B. subtilis*, *B. amyloliquefaciens*, *Bacillus pumilus* and *Bacillus gibsonii*, and *Cellulomonas* described in US 6,312,936 B1, US 5,679,630, US 4,760,025, US 5,030,378, WO 05/052146, DEA6022216A1 and DEA 6022224A1;

(b) trypsin-like proteases are trypsin (e.g., of porcine or bovine origin) and the *Fusarium* protease described in WO 89/06270; and

(c) metalloproteases, especially those derived from *Bacillus amyloliquefaciens* described in WO 07/044993A2. Preferred proteases are those derived from the BPN' and Carlsberg families, especially the subtilisin BPN' protease derived from *Bacillus amyloliquefaciens*. In one aspect, the protease is a variant of the subtilisin BPN' wild-type enzyme derived from *Bacillus amyloliquefaciens* that contains the Y217L mutation. The subtilisin BPN' wild-type enzyme sequence is the 275 amino acids (amino acids 108-382) of the Swissprot accession no. P00782 (derived from *Bacillus*

amyloliquefaciens). Preferred commercially available protease enzymes include those sold under the trade names Alcalase®, Savinase®, Primase®, Durazym®, Polarzymc®, Kannase®, Liquanase®, Ovozyme®, Neutrase®, Everlase® and Esperase® by Novozymes A/S (Denmark), those sold under the tradename Maxatase®, Maxacal®, Maxapem®, Properase®, Purafect®, Purafect Prime®, Purafect Ox®, FN3®, FN4®, Excellase® and Purafect OXP® by Genencor International, and those sold under the tradename Opticlean® and Optimise® by Solvay Enzymes. In one aspect, the preferred protease is that sold under the tradename Purafect Prime®, supplied by Genencor International.

19. Enzymes from E.C. 4.2.2.2 (pectate lyase). In one aspect the enzyme may comprise a pectate lyase. Suitable pectate lyases are described in WO 00/42151 and WO 00/42147. Preferred pectate lyases are sold under the tradenames Pectawash® and Pectaway® by Novozymes A/S.

20. Enzymes from E.C. 4.2.2.10 (pectin lyase).

Detergent surfactant

[0094] The composition comprises greater than 1wt% detergent surfactant, preferably from 10wt% to 40wt%, preferably from 12wt%, or from 15wt%, or even from 18wt% detergent surfactant. Preferably, the surfactant comprises alkyl benzene sulphonate and one or more detergent co-surfactants. The surfactant preferably comprises C₁₀-C₁₃ alkyl benzene sulphonate and one or more co-surfactants. The co-surfactants preferably are selected from the group consisting of C₁₂-C₁₈ alkyl ethoxylated alcohols, preferably having an average degree of ethoxylation of from 1 to 7; C₁₂-C₁₈ alkyl ethoxylated sulphates, preferably having an average degree of ethoxylation of from 1 to 5; and mixtures thereof. However, other

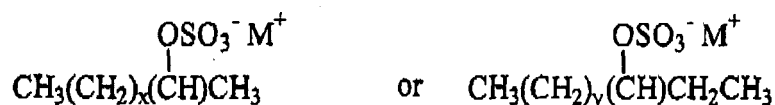
surfactant systems may be suitable for use in the present invention.

[0095] Suitable deterative surfactants include anionic deterative surfactants, nonionic deterative surfactants, cationic deterative surfactants, zwitterionic deterative surfactants, amphoteric deterative surfactants and mixtures thereof.

[0096] Suitable anionic deterative surfactants include: alkyl sulphates; alkyl sulphonates; alkyl phosphates; alkyl phosphonates; alkyl carboxylates; and mixtures thereof. The anionic surfactant can be selected from the group consisting of C₁₀-C₁₈ alkyl benzene sulphonates (LAS) preferably C₁₀-C₁₃ alkyl benzene sulphonates; C₁₀-C₂₀ primary, branched chain, linear-chain and random-chain alkyl sulphates (AS), typically having the following formula:



wherein, M is hydrogen or a cation which provides charge neutrality, preferred cations are sodium and ammonium cations, wherein x is an integer of at least 7, preferably at least 9; C₁₀-C₁₈ secondary (2,3) alkyl sulphates, typically having the following formulae:



wherein, M is hydrogen or a cation which provides charge neutrality, preferred cations include sodium and ammonium cations, wherein x is an integer of at least 7, preferably at least 9, y is an integer of at least 8, preferably at least 9; C₁₀-C₁₈ alkyl alkoxy carboxylates; mid-chain branched alkyl sulphates as described in more detail in US 6,020,303 and US 6,060,443; modified alkylbenzene sulphonate (MLAS) as described in more detail in WO 99/05243, WO 99/05242, WO 99/05244, WO 99/05082, WO 99/05084, WO 99/05241, WO 99/07656, WO 00/23549, and WO 00/23548; methyl ester sulphonate (MES); alpha-olefin sulphonate (AOS) and mixtures thereof.

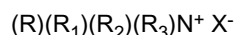
[0097] Preferred anionic deterative surfactants include: linear or branched, substituted or unsubstituted alkyl benzene sulphonate deterative surfactants, preferably linear C₈-C₁₈ alkyl benzene sulphonate deterative surfactants; linear or branched, substituted or unsubstituted alkyl benzene sulphate deterative surfactants; linear or branched, substituted or unsubstituted alkyl sulphate deterative surfactants, including linear C₈-C₁₈ alkyl sulphate deterative surfactants, C₁-C₃ alkyl branched C₈-C₁₈ alkyl sulphate deterative surfactants, linear or branched alkoxyated C₈-C₁₈ alkyl sulphate deterative surfactants and mixtures thereof; linear or branched, substituted or unsubstituted alkyl sulphonate deterative surfactants; and mixtures thereof.

[0098] Preferred alkoxyated alkyl sulphate deterative surfactants are linear or branched, substituted or unsubstituted C₈-C₁₈ alkyl alkoxyated sulphate deterative surfactants having an average degree of alkoxylation of from 1 to 30, preferably from 1 to 10. Preferably, the alkoxyated alkyl sulphate deterative surfactant is a linear or branched, substituted or unsubstituted C₈-C₁₈ alkyl ethoxyated sulphate having an average degree of ethoxylation of from 1 to 10. Most preferably, the alkoxyated alkyl sulphate deterative surfactant is a linear unsubstituted C₈-C₁₈ alkyl ethoxyated sulphate having an average degree of ethoxylation of from 3 to 7. Preferably, the laundry detergent composition comprises an alkyl ethoxyated sulphate having an average degree of ethoxylation of from 0.5 to 3.5, preferably from 1.0 to 3.0, and preferably 1.0 or 3.0.

[0099] Preferred anionic deterative surfactants are selected from the group consisting of: linear or branched, substituted or unsubstituted, C₁₂-C₁₈ alkyl sulphates; linear or branched, substituted or unsubstituted, C₁₀-C₁₃ alkylbenzene sulphonates, preferably linear C₁₀-C₁₃ alkylbenzene sulphonates; and mixtures thereof. Highly preferred are linear C₁₀-C₁₃ alkylbenzene sulphonates. Highly preferred are linear C₁₀-C₁₃ alkylbenzene sulphonates that are obtainable, preferably obtained, by sulphonating commercially available linear alkyl benzenes (LAB); suitable LAB include low 2-phenyl LAB, such as those supplied by Sasol under the tradename Isochem® or those supplied by Petresa under the tradename Petrelab®, other suitable LAB include high 2-phenyl LAB, such as those supplied by Sasol under the tradename Hyblene®. A suitable anionic deterative surfactant is alkyl benzene sulphonate that is obtained by DETAL catalyzed process, although other synthesis routes, such as HF, may also be suitable. Preferably, the laundry detergent composition comprises a predominantly C₁₂ alkyl sulphate.

[0100] Suitable cationic deterative surfactants include: alkyl pyridinium compounds; alkyl quaternary ammonium compounds; alkyl quaternary phosphonium compounds; alkyl ternary sulphonium compounds; and mixtures thereof. The cationic deterative surfactant can be selected from the group consisting of: alkoxyate quaternary ammonium (AQA) surfactants as described in more detail in US 6,136,769; dimethyl hydroxyethyl quaternary ammonium as described in more detail in US 6,004,922; polyamine cationic surfactants as described in more detail in WO 98/35002, WO 98/35003,

WO 98/35004, WO 98/35005, and WO 98/35006; cationic ester surfactants as described in more detail in US 4,228,042, US 4,239,660, US 4,260,529 and US 6,022,844; amino surfactants as described in more detail in US 6,221,825 and WO 00/47708, specifically amido propyldimethyl amine; and mixtures thereof. Preferred cationic deterative surfactants are quaternary ammonium compounds having the general formula:



wherein, R is a linear or branched, substituted or unsubstituted C₆₋₁₈ alkyl or alkenyl moiety, R₁ and R₂ are independently selected from methyl or ethyl moieties, R₃ is a hydroxyl, hydroxymethyl or a hydroxyethyl moiety, X is an anion which provides charge neutrality, preferred anions include halides (such as chloride), sulphate and sulphonate. Preferred cationic deterative surfactants are mono-C₆₋₁₈ alkyl mono-hydroxyethyl di-methyl quaternary ammonium chlorides. Highly preferred cationic deterative surfactants are mono-C₈₋₁₀ alkyl mono-hydroxyethyl di-methyl quaternary ammonium chloride, mono-C₁₀₋₁₂ alkyl mono-hydroxyethyl di-methyl quaternary ammonium chloride and mono-C₁₀ alkyl mono-hydroxyethyl di-methyl quaternary ammonium chloride.

[0101] Suitable non-ionic deterative surfactant can be selected from the group consisting of: C₈-C₁₈ alkyl ethoxylates, such as, NEODOL® non-ionic surfactants from Shell; C₆-C₁₂ alkyl phenol alkoxyates wherein the alkoxyate units are ethyleneoxy units, propyleneoxy units or a mixture thereof; C₁₂-C₁₈ alcohol and C₆-C₁₂ alkyl phenol condensates with ethylene oxide/propylene oxide block polymers such as Pluronic® from BASF; C₁₄-C₂₂ mid-chain branched alcohols, BA, as described in more detail in US 6,150,322; C₁₄-C₂₂ mid-chain branched alkyl alkoxyates, BAEx, wherein x = from 1 to 30, as described in more detail in US 6,153,577, US 6,020,303 and US 6,093,856; alkylpolysaccharides as described in more detail in US 4,565,647, specifically alkylpolyglycosides as described in more detail in US 4,483,780 and US 4,483,779; polyhydroxy fatty acid amides as described in more detail in US 5,332,528, WO 92/06162, WO 93/19146, WO 93/19038, and WO 94/09099; ether capped poly(oxyalkylated) alcohol surfactants as described in more detail in US 6,482,994 and WO 01/42408; and mixtures thereof.

[0102] The non-ionic deterative surfactant could be an alkyl polyglucoside and/or an alkyl alkoxyated alcohol. Preferably the non-ionic deterative surfactant is a linear or branched, substituted or unsubstituted C₈₋₁₈ alkyl ethoxyated alcohol having an average degree of ethoxylation of from 1 to 10, more preferably from 3 to 7.

Amphilic graft co-polymer

[0103] The laundry detergent composition preferably comprises an amphilic graft co-polymer, preferably the amphilic graft co-polymer comprises (i) polyethyleneglycol backbone; and (ii) and at least one pendant moiety selected from polyvinyl acetate, polyvinyl alcohol and mixtures thereof. A preferred amphilic graft co-polymer is Sokalan HP22, supplied from BASF.

Cellulosic based polymer

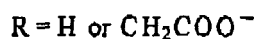
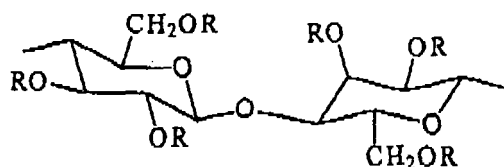
[0104] Preferably, the laundry detergent composition comprises cellulosic based polymer. The cellulosic based polymer can be any polymer that is or derived from cellulose. Suitable cellulosic based polymers include anionically modified celluloses, non-ionically modified celluloses, cationically modified celluloses, zwitterionically modified celluloses, and any mixture thereof. Suitable cellulosic based polymers can be both non-ionically modified and anionically modified, such as a cellulose that is modified by the incorporation of both an alkyl and a carboxymethyl substituent moiety.

[0105] The cellulosic based polymer is typically a cellulose or a modified cellulose. Suitable cellulosic based polymers include cellulose, cellulose ethers, cellulose esters, cellulose amides and mixtures thereof. Suitable cellulosic based polymers include anionically modified cellulose, nonionically modified cellulose, cationically modified cellulose, zwitterionically modified cellulose, and mixtures thereof. Suitable cellulosic based polymers include methyl cellulose, carboxymethyl cellulose, ethyl cellulose, hydroxyl ethyl cellulose, hydroxyl propyl methyl cellulose, ester carboxymethyl cellulose, and mixtures thereof.

[0106] Other suitable cellulosic based polymers include cationic cellulose and derivatives thereof. Suitable cationic cellulose is available from Amerchol Corp. (Edison, NJ, USA) in their Polymer JR™ and LR™ series of polymers. Other suitable cationic cellulose is the form of a salt of hydroxyethyl cellulose that is reacted with trimethyl ammonium substituted epoxide, such as that supplied by Amerchol Corp. under the tradename Polyquaternium 10™. Another suitable type of cationic cellulose includes the polymeric quaternary ammonium salts of hydroxyethyl cellulose reacted with lauryl dimethyl ammonium-substituted epoxide, such as that supplied by Amerchol Corp. under the tradename Polyquaternium 24™. Suitable cellulosic polymers are supplied by Amerchol Corp. under the tradename Polymer LM-200™. Other suitable cellulosic based polymers include methylhydroxyethyl cellulose TYLOSE MH50™, hydroxypropylmethyl cellulose METH-OCCEL F4M™. Other suitable cellulosic based polymers include: quaternary nitrogen-containing cellulose ethers, such as those described in more detail in US 3,962,418; and copolymers of etherified cellulose and starch, such as those

described in more detail in US 3,958,581.

[0107] Most preferably, the cellulosic based polymer is carboxy methyl cellulose, typically having the following general formula:



and wherein at least one R moiety is CH_2COO^- .

[0108] Preferred cellulosic based polymers are selected from the group consisting of: cellulose; carboxymethyl cellulose; methyl cellulose; ethyl cellulose; hydroxyethyl cellulose; alkyl cellulose; mixture of alkyl and carboxymethyl cellulose; and mixtures thereof. Highly preferred are carboxymethyl cellulose and/or methyl cellulose. Most preferred cellulosic based polymers are carboxymethyl cellulose.

Polymeric carboxylate

[0109] The composition preferably comprises polymeric carboxylate. It may be preferred for the composition to comprise at least 5wt% or at least 6wt%, or at least 7wt%, or at least 8wt%, or even at least 9wt%, by weight of the composition, of polymeric carboxylate. The polymeric carboxylate can sequester free calcium ions in the wash liquor. The carboxylate polymers can also act as soil dispersants and can provide an improved particulate stain removal cleaning benefit. Preferred polymeric carboxylates include: polyacrylates, preferably having a weight average molecular weight of from 1,000Da to 20,000Da; co-polymers of maleic acid and acrylic acid, preferably having a molar ratio of maleic acid monomers to acrylic acid monomers of from 1:1 to 1:10 and a weight average molecular weight of from 10,000Da to 200,000Da, or preferably having a molar ratio of maleic acid monomers to acrylic acid monomers of from 0.3:1 to 3:1 and a weight average molecular weight of from 1,000Da to 50,000Da.

Zeolite builder

[0110] Preferably, the composition comprise from 0wt% to 10wt% zeolite builder, preferably to 8wt%, or to 6wt%, or to 4wt%, or even to 2wt% zeolite builder. The composition may even be substantially free of zeolite builder, substantially free means "no deliberately added". Typical zeolite builders are zeolite A, zeolite P and zeolite MAP.

Phosphate builder

[0111] Preferably, the composition comprise from 0wt% to 10wt% phosphate builder, preferably to 8wt%, or to 6wt%, or to 4wt%, or even to 2wt% phosphate builder. The composition may even be substantially free of phosphate builder, substantially free means "no deliberately added". A typical phosphate builder is sodium tri-polyphosphate.

Source of carbonate

[0112] The composition may comprise a source of carbonate. Preferred sources of carbonate include sodium carbonate and/or sodium bicarbonate. A highly preferred source of carbonate is sodium carbonate. Sodium percarbonate may also be used as the source of carbonate. Preferably, the composition comprises from 0wt% to 10wt% sodium carbonate.

Other detergent ingredients

[0113] The composition typically comprises other detergent ingredients. Suitable detergent ingredients include: transition metal catalysts; enzymes such as amylases, carbohydrases, cellulases, laccases, lipases, bleaching enzymes such as oxidases and peroxidases, proteases, pectate lyases and mannanases; suds suppressing systems such as silicone based suds suppressors; brighteners; hueing agents; photobleach; fabric-softening agents such as clay, silicone

and/or quaternary ammonium compounds; flocculants such as polyethylene oxide; dye transfer inhibitors such as polyvinylpyrrolidone, poly 4-vinylpyridine N-oxide and/or co-polymer of vinylpyrrolidone and vinylimidazole; fabric integrity components such as oligomers produced by the condensation of imidazole and epichlorohydrin; soil dispersants and soil anti-redeposition aids such as alkoxylated polyamines and ethoxylated ethyleneimine polymers; anti-redeposition components such as polyesters; perfumes such as perfume microcapsules; soap rings; aesthetic particles; dyes; fillers such as sodium sulphate, although it is preferred for the composition to be substantially free of fillers; silicate salt such as sodium silicate, including 1.6R and 2.0R sodium silicate, or sodium metasilicate; co-polyesters of di-carboxylic acids and diols; cellulosic polymers such as methyl cellulose, carboxymethyl cellulose, hydroxyethoxycellulose, or other alkyl or alkylalkoxy cellulose; and any combination thereof.

Reserve alkalinity

[0114] Typically, the laundry detergent composition has a reserve alkalinity of at least 5.0, preferably at least 5.5, or at least 6.0, or at least 6.5, or at least 7.0, or at least 7.5, or at least 8.0, or at least 8.5, or at least 9.0, or at least 9.5, or at least 10.0, or at least 10.5, or at least 11.0, or at least 11.5, or at least 12.0, or at least 13, or at least 14, or at least 15, or at least 16, or at least 17, or at least 18, or at least 19, or at least 20. Preferably, the reserve alkalinity of the composition will not exceed 100.

[0115] As used herein, the term "reserve alkalinity" is a measure of the buffering capacity of the laundry detergent composition (g/NaOH/100g detergent composition) determined by titrating a 1% (w/v) solution of detergent composition with hydrochloric acid to pH 7.5 i.e in order to calculate Reserve Alkalinity as defined herein:

$$\text{Reserve Alkalinity (to pH 7.5) as \% alkali in g NaOH/100 g product} = \frac{T \times M \times 40 \times \text{Vol}}{10 \times \text{Wt} \times \text{Aliquot}}$$

T = titre (ml) to pH 7.5
 M = Molarity of HCl = 0.2
 40 = Molecular weight of NaOH
 Vol = Total volume (ie. 1000 ml)
 W = Weight of product (10 g)
 Aliquot = (100 ml)

[0116] Obtain a 10g sample accurately weighed to two decimal places, of fully formulated detergent composition. The sample should be obtained using a Pascall sampler in a dust cabinet. Add the 10g sample to a plastic beaker and add 200 ml of carbon dioxide-free de-ionised water. Agitate using a magnetic stirrer on a stirring plate at 150 rpm until fully dissolved and for at least 15 minutes. Transfer the contents of the beaker to a 1 litre volumetric flask and make up to 1 litre with deionised water. Mix well and take a 100 mls $\pm$ 1 ml aliquot using a 100 mls pipette immediately. Measure and record the pH and temperature of the sample using a pH meter capable of reading to ± 0.01 pH units, with stirring, ensuring temperature is 21 °C $\pm$ 2 °C. Titrate whilst stirring with 0.2M hydrochloric acid until pH measures exactly 7.5. Note the millilitres of hydrochloric acid used. Take the average titre of three identical repeats. Carry out the calculation described above to calculate RA to pH 7.5.

[0117] Preferably, the reserve alkalinity of the detergent composition will be greater than 7.5 and preferably greater than 8. The reserve alkalinity may be greater than 9 or even greater than 9.5 or 10 or higher. The RA may be up to 20 or higher.

[0118] Adequate reserve alkalinity may be provided, at least in part, for example, by one or more of alkali metal silicates (excluding crystalline layered silicate), typically amorphous silicate salts, generally 1.0 to 2.2 ratio sodium salts, alkali metal, typically sodium, carbonate, bicarbonate and/or sesquicarbonates, persalts such as perborates and percarbonates also contribute to alkalinity. Sodium percarbonate may also be used. Highly preferably, the laundry detergent composition comprises an alkalinity source selected from sodium metasilicate, sodium hydroxide, and mixtures thereof.

pH

[0119] Preferably, the laundry detergent composition has a pH of less than 11.0 at a concentration of 1 g/L in de-ionized water at a temperature of 20°C. Preferably the laundry detergent composition has a pH of less than 10.5, or less than 10.0, or even less than 9.5 at a concentration of 1 g/L in de-ionized water at a temperature of 20°C.

[0120] However, the laundry detergent may have a pH of at least 11.0 at a concentration of 1g/L in de-ionized water at a temperature of 20°C. If the laundry detergent composition has such higher pH profiles, then preferably the laundry detergent composition comprises greater than 10wt%, preferably greater than 12wt%, or greater than 15wt%, or greater than 17wt%, or greater than 20wt%, or greater than 22wt%, or greater than 25wt% alkalinity source.

[0121] Preferred alkalinity sources include: alkali metal silicates (excluding crystalline layered silicate), typically amorphous silicate salts, generally 1.0 to 2.2 ratio sodium salts; alkali metal, typically sodium, carbonate, bicarbonate and/or sesquicarbonates; persalts such as perborates and percarbonates also contribute to alkalinity; and mixture thereof. Sodium percarbonate may also be used. Highly preferably, the laundry detergent composition comprises an alkalinity source selected from sodium metasilicate, sodium hydroxide, and mixtures thereof.

[0122] The pH may be determining by dissolving or diluting the laundry detergent composition to a concentration of 1 g/L at a temperature of 20°C and determining the pH by any suitable method, such as using a pH meter.

EXAMPLES

[0123] 30g of the following free-flowing particulate laundry detergent compositions were used to wash 3.0kg fabric in a Miele 3622 front-loading automatic washing machine (13L wash liquor volume, short wash cycle (1h, 25mins), 12°C wash temperature).

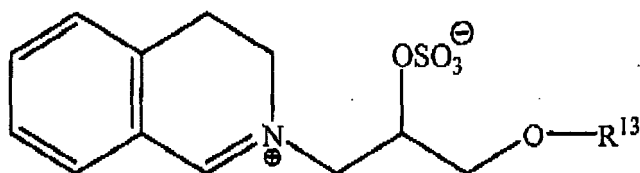
Ingredient	Composition A	Composition B	Composition C	Composition D
Bleaching ingredient*	0.05wt%	0.1wt%	0.05wt%	0.01wt%
Tetraacetythylenediamine (TAED)	10.0wt%	7.5wt%	12wt%	10wt%
Coated sodium percarbonate (PC3)	10.0wt%	15wt%	12wt%	10wt%
Hydroxyethane di[methylenephosphonic acid] (HEDP)	0.5wt%	0.5wt%	0.1wt%	0.8wt%
C ₁₁₋₁₃ alkyl benzene sulphonate (LAS)	20.0wt%	25wt%	15wt%	20wt%
Ethoxylated C ₁₂₋₁₅ alkyl sulphate having average degree of ethoxylation of between 1 and 3 (AE ₁₋₃ S)	5.0wt%	5wt%	10wt%	7wt%
mono-C ₈₋₁₀ alkyl mono-hydroxyethyl dimethyl quaternary ammonium chloride	1.0wt%	0.5wt%	2.0wt%	1.5wt%
Sodium sulphate	3.0wt%	0wt%	0wt%	1wt%
Sodium carbonate	25.0wt%	20wt%	30wt%	22wt%
Sodium silicate (1.6R)	2.0wt%	0wt%	0wt%	1.0wt%
Zeolite 4A	2.0wt%	0wt%	0wt%	1.0wt%
Florescent whitening agent	0.5wt%	0.5wt%	0.1wt%	0.5wt%
Silicone suds suppressor	0.05wt%	0.05wt%	0.1wt%	0.05wt%
Enzymes (protease, amylase, cellulase and mixtures thereof)	2.0wt%	1.0wt%	1.5wt%	2.0wt%
Co-polymer of maleic acid and acrylic acid (MA/AA)	8.0wt%	10wt%	12wt%	10wt%
Polyethylene oxide with pendant polyvinylacetate groups	2.0wt%	4.0wt%	1.0wt%	1.5wt%
Carboxymethyl cellulose (CMC)	1.0wt%	2.0wt%	1.0wt%	1.2wt%
Repel-o-tex	0.1wt%	0wt%	0.2wt%	0.15wt%
Moisture & Miscellaneous	to 100wt%	to 100wt%	to 100wt%	to 100wt%
* bleach ingredient is sulphuric acid mono-[2-(3,4-dihydro-isoquinolin-2-yl)-1-(2-butyl-octyloxymethyl)-ethyl] ester, internal salt.				

Claims

1. A method of laundering fabric comprising the step of contacting a laundry detergent composition to water to form a wash liquor, and laundering fabric in said wash liquor, wherein the wash liquor has a temperature of above 0°C to 20°C, and wherein the laundry detergent composition comprises greater than 1wt% deterative surfactant and other detergent ingredients.

2. A method according to claim 1, wherein the laundry detergent composition comprises a bleach ingredient selected from:

(a) bleach ingredient having a $\log P_{o/w}$ of no greater than about 0, wherein the bleach ingredient is capable of generating species having a X_{SO} of from about 0.01 to about 0.30, and preferably having a structure corresponding to general formula below:



wherein R^{13} is selected from the group consisting of 2-ethylhexyl, 2-propylheptyl, 2-butyloctyl, 2-pentylononyl, 2-hexyldecyl, n-dodecyl, n-tetradecyl, n-hexadecyl, n-octadecyl, iso-nonyl, iso-decyl, iso-tridecyl and iso-pentadecyl; and/or

(b) transition metal bleach catalyst; and/or

(c) pre-formed peracid; and/or

(d) coated source of hydrogen peroxide,

preferably the bleach ingredient is encapsulated or coated, and preferably the laundry detergent composition comprises from above 0wt% to 10wt% source of hydrogen peroxide.

3. A method according to any preceding claim, wherein the laundry detergent composition comprises a layered particle, wherein the layered particle comprises a core and a layer, wherein the core comprises a source of hydrogen peroxide, wherein the layer comprises a binder and a bleach activator, and wherein the weight ratio of the source of hydrogen peroxide to the bleach activator present in the layered particle is in the range of from about 5:1 to about 1.1:1.

4. A method according to any preceding claim, wherein the laundry detergent composition comprises a chelent selected from:

(a) ethylene diamine-N'N'-disuccinic acid or salt thereof (EDDS); and/or

(b) 4,5-dihydroxy-m-benzenedisulfonic acid disodium salt.

5. A method according to any preceding claim, wherein the laundry detergent composition comprises hueing agent.

6. A method according to any preceding claim, wherein the laundry detergent composition comprises enzyme.

7. A method according to any preceding claim, wherein the laundry detergent composition has one of the following features:

(a) a reserve alkalinity of 5 or greater; and/or

(b) a pH of less than 11.0 at a concentration of 1g/L in de-ionized water at a temperature of 20°C; or

(c) comprises greater than 10.0wt% alkalinity source, and has a pH of at least 11.0 at a concentration of 1g/L in de-ionized water at a temperature of 20°C.

8. A method according to any preceding claim, wherein the laundry detergent composition comprises:

- (a) from 0wt% to less than 10wt% zeolite builder; and
- (b) from 0wt% to less than 10wt% phosphate builder.

9. A method according to any preceding claim, wherein the laundry detergent composition comprises deterative surfactant selected from:

- (a) alkyl ethoxylated sulphate having an average degree of ethoxylation of from 0.5 to 3.5; and/or
- (b) predominantly C₁₂ alkyl sulphate.

10. A method according to any preceding claim, wherein the laundry detergent composition comprises polymer selected from:

(a) an amphilic graft polymer, preferably the amphilic graft polymer comprises:

- (i) polyethylene glycol backbone; and
- (ii) at least one pendant moiety selected from polyvinyl acetate, polyvinyl alcohol and mixtures thereof; and/or

(b) cellulosic based polymer, preferably carboxymethyl cellulose; and/or

(c) polymeric carboxylate; and/or

(d) cationic polymer.

11. A method according to any preceding claim, wherein the laundry detergent composition comprises perfume microcapsule.

12. A method according to any preceding claim, wherein the laundry detergent composition is in a form selected from:

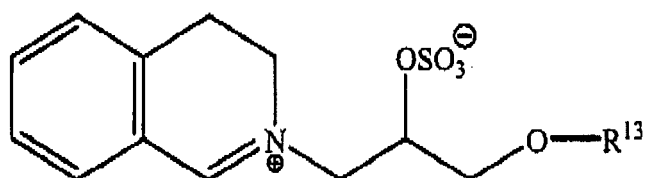
- (a) solid; and/or
- (b) liquid; and/or
- (c) unit dose.

13. A method according to any preceding claim, wherein the laundry detergent composition comprises from 0wt% to 40wt% water, preferably from 0wt% to 20wt% water, more preferably from 0wt% to 10wt% water.

14. A method according to any preceding claim, wherein the wash liquor has a temperature of from above 0°C to 15°C, preferably from 0°C to 10°C.

15. Use of a catalytic ingredient to improve the cleaning performance and/or hygiene profile of a laundry detergent composition during a laundering process at a temperature of from above 0°C to 20°C, preferably the catalytic ingredient is selected from:

- (a) transition metal catalyst; and/or
- (b) bleach catalyst having a structure corresponding to general formula below:



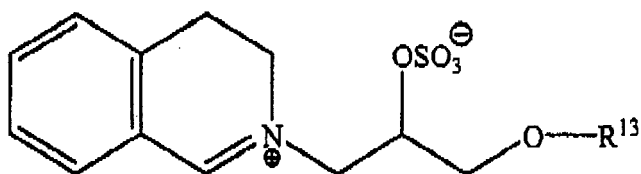
wherein R¹³ is selected from the group consisting of 2-ethylhexyl, 2-propylheptyl, 2-butyloctyl, 2-pentylononyl, 2-hexyldecyl, n-dodecyl, n-tetradecyl, n-hexadecyl, n-octadecyl, iso-nonyl, iso-decyl, iso-tridecyl and iso-pentadecyl; and/or

(c) enzyme.

16. A method of laundering fabric comprising the step of contacting a solid laundry detergent composition to water to

form a wash liquor, and laundering fabric in said wash liquor, wherein the wash liquor has a temperature of above 0°C to 20°C, and wherein the solid laundry detergent composition comprises:

- (a) alkyl ethoxylated sulphate having an average degree of ethoxylation of from 0.5 to 3.5;
- (b) from 0wt% to 10wt% zeolite builder;
- (c) from 0wt% to 10wt% phosphate builder;
- (d) enzyme;
- (e) bleach catalyst having a structure corresponding to general formula below:



wherein R^{13} is selected from the group consisting of 2-ethylhexyl, 2-propylheptyl, 2-butyloctyl, 2-pentylononyl, 2-hexyldecyl, n-dodecyl, n-tetradecyl, n-hexadecyl, n-octadecyl, iso-nonyl, iso-decyl, iso-tridecyl and iso-pentadecyl;

(f) layered particle, wherein the layered particle comprises a core and a layer, wherein the core comprises a source of hydrogen peroxide, wherein the layer comprises a binder and a bleach activator, and wherein the weight ratio of the source of hydrogen peroxide to the bleach activator is from about 5:1 to about 1.1:1;

(g) optionally, transition metal bleach catalyst;

(h) optionally, hueing agent; and

(i) optionally, from 0wt% to 10wt% sodium carbonate.



EUROPEAN SEARCH REPORT

Application Number
EP 09 01 0447

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	US 2006/089284 A1 (MIRACLE GREGORY S [US] ET AL) 27 April 2006 (2006-04-27) * paragraphs [0002] - [0005], [0016], [0017], [0030], [0031], [0033] - [0038], [0064]; claims; examples *	1-16	INV. C11D11/00 C11D3/00 C11D3/39 C11D3/34 C11D3/16 C11D3/386 C11D1/29
X	US 2004/018951 A1 (MIRACLE GREGORY S [US] ET AL) 29 January 2004 (2004-01-29) * paragraphs [0003] - [0005], [0119], [0127], [0128], [0130] - [0135], [0138], [0140], [0173]; claims; example 17 *	1-16	
X	EP 1 036 840 A (KAO CORP [JP]) 20 September 2000 (2000-09-20) * paragraph [0003]; examples *	1-16	
X	WO 98/59024 A (PROCTER & GAMBLE [US]) 30 December 1998 (1998-12-30) * page 1, lines 7-13 * * page 2, lines 19-28 * * page 8, lines 12-17 * * examples *	1-16	TECHNICAL FIELDS SEARCHED (IPC) C11D
X	EP 0 158 464 A (CLOROX CO [US]) 16 October 1985 (1985-10-16) * page 4, line 12 - page 6, line 27 * * page 16, lines 6-16 * * page 17, line 16 - page 18, line 19 * * examples *	1-16	
X	US 4 743 394 A (KAUFMANN EDWARD J [US] ET AL) 10 May 1988 (1988-05-10) * column 4, lines 29-62 * * column 10, lines 28-44 * * column 11, lines 16-68 * * claims; examples *	1-16	
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 22 January 2010	Examiner Péntek, Eric
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

 3
EPO FORM 1503 03.82 (P04C01)



EUROPEAN SEARCH REPORT

Application Number
EP 09 01 0447

DOCUMENTS CONSIDERED TO BE RELEVANT				
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)	
X	US 5 482 646 A (MAZZOLA LOUIS R [US]) 9 January 1996 (1996-01-09) * column 2, lines 24-31; examples * -----	1-16		
X	US 6 274 545 B1 (MAZZOLA LOUIS R [US]) 14 August 2001 (2001-08-14) * column 1, lines 13-20 * * column 1, lines 55-64 * * column 3, lines 48-57 * * column 5, lines 39-48 * * examples * -----	1-16		
X	GB 2 289 687 A (PROCTER & GAMBLE [US]) 29 November 1995 (1995-11-29) * page 1, lines 7-17 * * page 4, line 15 - page 5, line 7 * * page 11, lines 13-20 * * examples * -----	1-16		
X	US 5 945 394 A (SAJIC BRANKO [US] ET AL) 31 August 1999 (1999-08-31) * column 11, line 19 - column 19, line 42; examples * -----	1-16		TECHNICAL FIELDS SEARCHED (IPC)
X	GB 1 013 394 A (PROCTER & GAMBLE) 15 December 1965 (1965-12-15) * claims; examples * -----	1-16		
X	FR 1 059 696 A (CHEMISCHE WERKE ALBERT) 26 March 1954 (1954-03-26) * page 1, left-hand column, lines 21-26 * * page 1, left-hand column, line 33 - page 2, left-hand column, line 32 * * claims; examples * -----	1-16		
The present search report has been drawn up for all claims				
Place of search Munich		Date of completion of the search 22 January 2010	Examiner Péntek, Eric	
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document				

 3
EPO FORM 1503 03.02 (P04C01)



EUROPEAN SEARCH REPORT

Application Number
EP 09 01 0447

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	FR 1 115 755 A (BEAL ANDRÉ) 30 April 1956 (1956-04-30) * page 1, left-hand column, line 11 - page 2, left-hand column, line 31; claims *	1-16	
X	EP 0 890 635 A (MANITOBA ITALIA SPA [IT]) 13 January 1999 (1999-01-13) * page 2, lines 38-52 * * page 4, line 17 - page 15, line 10 * * claims *	1-16	
			TECHNICAL FIELDS SEARCHED (IPC)
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 22 January 2010	Examiner Péntek, Eric
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

3
EPO FORM 1503 03.82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 09 01 0447

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

22-01-2010

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2006089284 A1	27-04-2006	US 2009222999 A1	10-09-2009
US 2004018951 A1	29-01-2004	US 2009143272 A1	04-06-2009
		US 2006211590 A1	21-09-2006
EP 1036840 A	20-09-2000	CN 1267716 A	27-09-2000
		DE 60022111 D1	29-09-2005
		DE 60022111 T2	22-06-2006
		ES 2243163 T3	01-12-2005
		US 6197740 B1	06-03-2001
WO 9859024 A	30-12-1998	BR 9810933 A	26-09-2000
		CA 2293569 A1	30-12-1998
		CN 1261398 A	26-07-2000
		EP 0991742 A1	12-04-2000
		JP 2002506471 T	26-02-2002
		MA 24666 A1	01-07-1999
EP 0158464 A	16-10-1985	AR 241466 A1	31-07-1992
		AU 575383 B2	28-07-1988
		AU 4025885 A	26-09-1985
		BR 8501303 A	19-11-1985
		CA 1284602 C	04-06-1991
		DE 3571643 D1	24-08-1989
		EG 16786 A	30-08-1991
		ES 8705022 A1	01-07-1987
		ES 8801714 A1	16-04-1988
		ES 8801363 A1	01-03-1988
		JP 60212495 A	24-10-1985
		MX 164019 B	09-07-1992
		TR 22756 A	14-06-1988
US 4743394 A	10-05-1988	NONE	
US 5482646 A	09-01-1996	NONE	
US 6274545 B1	14-08-2001	NONE	
GB 2289687 A	29-11-1995	NONE	
US 5945394 A	31-08-1999	NONE	
GB 1013394 A	15-12-1965	BE 660644 A	06-09-1965
		NL 290951 A	
FR 1059696 A	26-03-1954	BE 512527 A	

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 09 01 0447

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

22-01-2010

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
FR 1115755	A	30-04-1956	FR	69094 E	22-09-1958
EP 0890635	A	13-01-1999	IT	MI971617 A1	08-01-1999

REFERENCES CITED IN THE DESCRIPTION

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

Patent documents cited in the description

- US 5360569 A [0023]
- US 5360568 A [0023]
- US 5576282 A [0024] [0047]
- US 5817614 A [0024]
- WO 05047264 A [0024]
- US 5753599 A [0029]
- US 6649085 B [0031]
- US 5580485 A [0046]
- US 4430243 A [0046]
- US 4728455 A [0046]
- US 5246621 A [0046]
- US 5244594 A [0046]
- US 5284944 A [0046]
- US 5194416 A [0046]
- US 5246612 A [0046]
- US 5256779 A [0046]
- US 5280117 A [0046]
- US 5274147 A [0046]
- US 5153161 A [0046]
- US 5227084 A [0046]
- US 5114606 A [0046]
- US 5114611 A [0046]
- EP 549271 A1 [0046]
- EP 544490 A1 [0046]
- EP 549272 A1 [0046]
- EP 544440 A2 [0046]
- US 5597936 A [0048]
- US 5595967 A [0048]
- WO 05042532 A1 [0049]
- US 4915854 A, Mao [0065]
- US 4412934 A [0065]
- US 4634551 A [0065] [0067]
- US 4966723 A, Hodge [0068]
- US 4545784 A, Sanderson [0069]
- US 7208459 B2 [0091]
- WO 06002955 A2 [0093]
- US P7153818 B [0093]
- WO 9700324 A [0093]
- EP 1022334 A [0093]
- WO 9402597 A [0093]
- WO 9418314 A [0093]
- WO 9623874 A [0093]
- WO 9743424 A [0093]
- US P5856164 A [0093]
- WO 9923211 A [0093]
- WO 9623873 A [0093]
- WO 0060060 A [0093]
- WO 06002643 A [0093]
- US 44353077 B [0093]
- US 5648263 A [0093]
- US 5691178 A [0093]
- US 5776757 A [0093]
- WO 8909259 A [0093]
- EP 0495257 A [0093]
- EP 0531372 A [0093]
- WO 9611262 A [0093]
- WO 9629397 A [0093]
- WO 9808940 A [0093]
- WO 9407998 A [0093]
- EP 0531315 A [0093]
- US 5457046 A [0093]
- US 5686593 A [0093]
- US 5763254 A [0093]
- WO 9524471 A [0093]
- WO 9812307 A [0093]
- WO 9901544 A [0093]
- WO 01062903 A [0093]
- WO 2001062903 A [0093]
- WO 9909126 A [0093]
- WO 9964573 A [0093]
- WO 9909128 A [0093]
- US 6312936 B1 [0093]
- US 5679630 A [0093]
- US 4760025 A [0093]
- US 5030378 A [0093]
- WO 05052146 A [0093]
- DE A6022216 A1 [0093]
- DE A6022224 A1 [0093]
- WO 8906270 A [0093]
- WO 07044993 A2 [0093]
- WO 0042151 A [0093]
- WO 0042147 A [0093]
- US 6020303 A [0096] [0101]
- US 6060443 A [0096]
- WO 9905243 A [0096]
- WO 9905242 A [0096]
- WO 9905244 A [0096]
- WO 9905082 A [0096]
- WO 9905084 A [0096]
- WO 9905241 A [0096]
- WO 9907656 A [0096]
- WO 0023549 A [0096]
- WO 0023548 A [0096]
- US 6136769 A [0100]
- US 6004922 A [0100]
- WO 9835002 A [0100]
- WO 9835003 A [0100]
- WO 9835004 A [0100]

EP 2 292 725 A1

- WO 9835005 A [0100]
- WO 9835006 A [0100]
- US 4228042 A [0100]
- US 4239660 A [0100]
- US 4260529 A [0100]
- US 6022844 A [0100]
- US 6221825 B [0100]
- WO 0047708 A [0100]
- US 6150322 A [0101]
- US 6153577 A [0101]
- US 6093856 A [0101]
- US 4565647 A [0101]
- US 4483780 A [0101]
- US 4483779 A [0101]
- US 5332528 A [0101]
- WO 9206162 A [0101]
- WO 9319146 A [0101]
- WO 9319038 A [0101]
- WO 9409099 A [0101]
- US 6482994 B [0101]
- WO 0142408 A [0101]
- US 3962418 A [0106]
- US 3958581 A [0106]

Non-patent literature cited in the description

- *Tetrahedron*, 1992, vol. 49 (2), 423-38 [0023]
- *Tetrahedron Letters*, 1987, vol. 28 (48), 6061-6064 [0025]
- *Journal of Organic Chemistry*, 1990, vol. 55 (4), 1254-61 [0026]
- *Journal of the Chemical Society, Chemical Communications*, 1994, 2569-70 [0027]
- *Polish Journal of Chemistry*, 2003, vol. 77 (5), 577-590 [0028]
- *Tetrahedron Letters*, 1994, vol. 35 (34), 6329-30 [0030]
- **Brooke, D. N. ; Dobbs, A. J. ; Williams, N.** *Ecotoxicology and Environmental Safety*, 1986, vol. 11 (3), 251-260 [0038]
- **Adam, W. ; Haas, W. ; Lohray, B. B.** *Journal of the American Chemical Society*, 1991, vol. 113 (16), 6202-6208 [0039]
- *Acta Biochimica et Biophysica Sinica*, 2007, vol. 39 (11), 811-828 [0093]