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(57) Abstract: The present invention relates to a method of laundering fabric comprising the step of contacting a liquid laundry detergent composition comprising a pre-formed peracid, wherein the laundry detergent is contacted to water in such an amount so that the concentration of laundry detergent composition in the wash liquor is from above 0g/l to 4g/l, and wherein from 0.01kg to 2kg of fabric per litre of wash liquor is dosed into said wash liquor.

1

METHOD OF LAUNDERING FABRIC USING A LIQUID LAUNDRY DETERGENT COMPOSITION

FIELD OF THE INVENTION

The present invention relates to a method of laundering fabric. The method exhibits good bleach performance and has an excellent environmental profile.

BACKGROUND OF THE INVENTION

As one wishes to remove more and more chemistry from liquid laundry detergent products, one must optimize the cleaning performance of what is left or suffer a severe reduction in cleaning performance. This is especially true for bleaching performance.

As one removes more and more hydrogen peroxide source, less hydrogen peroxide is available to be converted into a perhydroxyl anion, and in turn (in the presence of decreasing levels of bleach activators) less peracid is available to contribute to bleaching performance. In addition to this, as one removes more and more alkalinity source, the reserve alkalinity of the detergent product is reduced, which in turn means that that the pH of the wash liquor is likely to reduce, which in turn reduces the proportion of hydrogen peroxide that exists as a perhydroxyl anion.

What remains constant though is the amount of fabric typically laundered during the washing process. So less bleach is used to clean the same amount of fabric. In addition, as well as being the substrate to be cleaned, this fabric brings in its own stress on the bleaching system, namely in the form of catalase, which is present in the fabric to be laundered, and rapidly catalyzses the decomposition of hydrogen peroxide to water and oxygen, thereby reducing the performance of the bleaching system.

The inventors have found that by incorporating a pre-formed peracid into the laundry detergent composition, one can maintain a good bleaching performance whilst at the same time compact the formulation and the bleach system.

The inventors herein provide a method of laundering fabric having a good bleach performance profile, whilst at the same time having a good environmental profile.

SUMMARY OF THE INVENTION

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

DETAILED DESCRIPTION OF THE INVENTION

2

Method of laundering fabric. The method of laundering fabric comprises the step of contacting a liquid laundry detergent composition comprising a pre-formed peracid to water to form a wash liquor, and laundering fabric in said wash liquor. The fabric may be contacted to the water prior to, or after, or simultaneous with, contacting the laundry detergent composition with water.

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 4g/l, preferably from 1g/l, and preferably to 3.5g/l, or to 3.0g/l, or to 2.5g/l, or to 2.0g/l, or even to 1.0g/l, or even to 0.5g/l.

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. 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.

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 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 even from 5 litres of water.

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, 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.

Preferably 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.

Preferably, the laundry detergent composition is contacted to 12 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 or less, or even to 6 litres or less of water to form the wash liquor.

3

Laundry detergent composition. The laundry detergent composition comprises a preformed peracid, and optionally other detergent ingredients. The pre-formed peracid is described in more detail below.

The composition can be any liquid form, for example a liquid or gel form, or any combination thereof. The composition may be in any unit dose form, for example a pouch. However, it is extremely highly preferred for the composition to be in gel form.

The composition is a fully finished laundry detergent composition. The composition is not just a component of a laundry detergent composition that can be incorporated into a laundry detergent composition: 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.

Pre-formed peroxyacid or salt thereof. The pre-peroxyacid or salt thereof is typically either a peroxycarboxylic acid or salt thereof, or a peroxysulphonic acid or salt thereof.

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:

$$\begin{array}{cccc}
O & & & \\
\parallel & & & \\
R^{14} - C - O - O & & Y
\end{array}$$

wherein: R^{14} is selected from alkyl, aralkyl, cycloalkyl, aryl or heterocyclic groups; the R^{14} 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, R^{14} is a linear or branched, substituted or unsubstituted C_{6-9} alkyl. Preferably, the peroxyacid or salt thereof is selected from peroxyhexanoic acid, peroxyheptanoic acid, peroxyoctanoic acid, peroxynonanoic acid, peroxydecanoic 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.

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:

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wherein: R^{15} is selected from alkyl, aralkyl, cycloalkyl, aryl or heterocyclic groups; the R^{15} 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 R^{15} is a linear or branched, substituted or unsubstituted C_{6-9} alkyl.

A highly preferred pre-formed peracid is phthalimido peroxy caproic acid. Phthalimido peroxycaproic acid is also known as: N, N-phthalimido peroxycaproic acid; 2H-Isoindole-2-hexaneperoxoic acid, 1,3-dihydro-1,3-dioxo-; 5-(Phthalimido)percaproic acid; 6-(Phthalimidoperoxy)hexanoic acid; 6-Phthalimidohexaneperoxoic acid; Eureco; Eureco HC; Eureco HCL 11; Eureco HCL 17; Eureco LX; Eureco W; Phthalimidoperhexanoic acid; e-(Phthalimidoperoxy)hexanoic acid; and 1,3-dihydro-1,3-dioxo-2H-Isoindole-2-hexaneperoxoic aci. The CAS number is 128275-31-0.

Phthalimido peroxycaproic acid has the following chemical structure:

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.

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.

5

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.

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.

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 preformed 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.

6

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. The particles are typically suspended within a continuous liquid phase. 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.

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.

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.

Bleach activator. 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 tetraacetylethylenediamine (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).

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

$$R^1N(R^5)C(O)R^2C(O)L \qquad \text{ or } \qquad R^1C(O)N(R^5)R^2C(O)L$$

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.

7

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

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:

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 R⁶ 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.

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

8

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.

Bleach catalyst. The composition may comprise bleach catalyst. Preferred bleach catalysts include oxaziridinium-based bleach catalysts, transition metal bleach catalysts, bleaching enzymes, and any combination thereof.

A highly preferred bleach catalyst 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 oxidizeable 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.

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).

Suitable iminium zwitterions include, but are not limited to, N-(3-sulfopropyl)-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.

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.

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.

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

9

amide, which can be made according to the procedures described in the Journal of the Chemical Society, Chemical Communications (1994), (22), 2569-70.

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.

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).

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.

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).

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.

Preferably, the bleach catalyst has a chemical structure corresponding to the following chemical formula

$$R^{1}_{(n)} \xrightarrow{R^{2}_{(m)}} X$$

wherein; n and m are independently from 0 to 4, preferably n and m are both 0; each R¹ is independently selected from a substituted or unsubstituted radical selected from the group consisting of hydrogen, alkyl, cycloalkyl, aryl, fused aryl, heterocyclic ring, fused heterocyclic ring, nitro, halo, cyano, sulphonato, alkoxy, keto, carboxylic, and carboalkoxy radicals; and any two vicinal R¹ substituents may combine to form a fused aryl, fused carbocyclic or fused heterocyclic ring; each R² is independently selected from a substituted or unsubstituted radical independently selected from the group consisting of hydrogen, hydroxy, alkyl, cycloalkyl, alkaryl, aryl, aralkyl, alkylenes, heterocyclic ring, alkoxys, arylcarbonyl groups, carboxyalkyl groups and amide groups; any R² may be joined together with any other of R² to form part of a common ring; any geminal R² may combine to form a carbonyl; and any two R² may combine to form a substituted or unsubstituted fused unsaturated moiety; R³ is a C₁ to C₂₀ substituted or unsubstituted alkyl; R⁴ is hydrogen or the moiety O_t-A, wherein: O is a branched or unbranched alkylene, t = 0 or 1 and A is an anionic group selected from the group consisting of OSO₃, SO₃, CO₂⁻, OCO₂⁻, OPO₃²⁻, OPO₃H⁻ and OPO₂⁻; R⁵ is hydrogen or the moiety -CR¹¹R¹²-Y-G_b-Y_c-[(CR⁹R¹⁰)_v-O]_k-R⁸, wherein: each Y is independently selected from the group consisting of O, S, N-H, or N-R⁸; and each R⁸ is independently selected from the group consisting of alkyl, aryl and heteroaryl, said moieties being substituted or unsubstituted, and whether substituted or unsubstituted said moieties having less than 21 carbons; each G is independently selected from the group consisting of CO, SO₂, SO, PO and PO₂; R⁹ and R¹⁰ are independently selected from the group consisting of H and C₁-C₄ alkyl; R¹¹ and R¹² are independently selected from the group consisting of H and alkyl, or when taken together may join to form a carbonyl; b = 0 or 1; c can = 0 or 1, but c must = 0 if b = 0; y is an integer from 1 to 6; k is an integer from 0 to 20; R^6 is H, or an alkyl, aryl or heteroaryl moiety; said moieties being substituted or unsubstituted; and X, if present, is a suitable charge balancing counterion, preferably X is present when R⁴ is hydrogen, suitable X, include but are not limited to: chloride, bromide, sulphate, methosulphate, sulphonate, p-toluenesulphonate, borontetraflouride and phosphate.

11

In one embodiment of the present invention, the bleach catalyst has a structure corresponding to general formula below:

$$OSO_3^{\Theta}$$

$$O-R^{12}$$

wherein R¹³ is a branched alkyl group containing from three to 24 carbon atoms (including the branching carbon atoms) or a linear alkyl group containing from one to 24 carbon atoms; preferably R¹³ is a branched alkyl group containing from eight to 18 carbon atoms or linear alkyl group containing from eight to eighteen carbon atoms; preferably R¹³ is selected from the group consisting of 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; preferably R¹³ is selected from the group consisting of 2-butyloctyl, 2-pentylnonyl, 2-hexyldecyl, iso-tridecyl and iso-pentadecyl.

In another embodiment of the present invention, the bleach catalyst has a structure corresponding to general formula below or mixtures thereof.

$$R^2$$
 R^2 R^2

wherein: G is selected from -O-, -CH₂O-, -(CH₂)₂-, and -CH₂-. R^1 is selected from H or C_1 - C_4 alkyl. Suitable C_1 - C_4 alkyl moieties include, but are not limited to methyl, ethyl, iso-propyl, and tert-butyl. Each R^2 is independently selected from C_4 - C_8 alkyl, benzyl, 2-methylbenzyl, 3-methylbenzyl, 4-methylbenzyl, 4-ethylbenzyl, 4-iso-propylbenzyl and 4-tert-butylbenzyl. Suitable C_4 - C_8 alkyl moieties include, but are not limited to n-butyl, n-pentyl, cyclopentyl, n-hexyl, cyclohexyl, cyclohexylmethyl, n-heptyl and octyl.

In one aspect of the invention G is selected from -O- and -CH₂-. R^1 is selected from H, methyl, ethyl, iso-propyl, and tert-butyl. Each R^2 is independently selected from C₄-C₆ alkyl, benzyl, 2-methylbenzyl, 3-methylbenzyl, and 4-methylbenzyl.

12

In another aspect of the invention G is $-CH_2$ -, R^1 is H and each R^2 is independently selected from n-butyl, n-pentyl, n-hexyl, benzyl, 2-methylbenzyl, 3-methylbenzyl, and 4-methylbenzyl.

Preferably, the composition comprises oxaziridinium-based bleach catalyst having the formula:

wherein: R¹ is selected from the group consisting of: H, a branched alkyl group containing from 3 to 24 carbons, and a linear alkyl group containing from 1 to 24 carbons; preferably, R¹ is a branched alkyl group comprising from 6 to 18 carbons, or a linear alkyl group comprising from 5 to 18 carbons, more preferably each R¹ is selected from the group consisting of: 2-propylheptyl, 2-butyloctyl, 2-pentylnonyl, 2-hexyldecyl, n-hexyl, n-octyl, n-decyl, n-dodecyl, n-tetradecyl, n-hexadecyl, n-octadecyl, iso-nonyl, iso-decyl, iso-tridecyl and iso-pentadecyl; R² is independently selected from the group consisting of: H, a branched alkyl group comprising from 3 to 12 carbons, and a linear alkyl group comprising from 1 to 12 carbons; preferably R² is independently selected from H and methyl groups; and n is an integer from 0 to 1.

Another suitable bleach catalyst is a transition metal bleach catalyst. Preferred transition metal bleach catalysts comprise manganese and/or iron.

Source of hydrogen peroxide. It is preferred that the composition is essentially free of (i.e. comprises no deliberately added) source of hydrogen peroxide, and the bleaching performance profile is delivered by the pre-formed peroxyacid or salt thereof, optionally in combination with bleach catalysts. However, it is within the scope of the present invention for some conventional bleaching ingredients, such as a source of hydrogen peroxide and/or a bleach catalyst to be present in the composition.

The composition may comprise 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% source of hydrogen peroxide. The wash liquor may comprise from above 0g/l to 0.5g/l hydrogen peroxide, preferably from 0.1g/l, and preferably to 0.4g/l, or even to 0.3g/l. The laundry detergent composition may comprise a source of hydrogen peroxide

13

in an amount such that during the method of the present invention from above 0g to 0.5g source of hydrogen peroxide per litre of water is contacted to said water when forming the wash liquor.

Preferred sources of hydrogen peroxide include sodium perborate, preferably in monohydrate or tetra-hydrate form or mixtures thereof, sodium percarbonate. Especially preferred is sodium percarbonate.

The detersive surfactant typically comprises anionic detersive surfactant and non-ionic surfactant, wherein preferably the weight ratio of anionic detersive surfactant to non-ionic detersive surfactant is greater than 1:1, preferably greater than 1.5:1, or even greater than 2:1, or even greater than 2:1, or greater than 3:1.

The composition preferably comprises detersive surfactant, preferably from 10wt% to 40wt%, preferably from 12wt%, or from 15wt%, or even from 18wt% detersive surfactant. Preferably, the surfactant comprises alkyl benzene sulphonate and one or more detersive cosurfactants. The surfactant preferably comprises C_{10} - C_{13} alkyl benzene sulphonate and one or more co-surfactants. The co-surfactants preferably are selected from the group consisting of C_{12} - C_{18} alkyl ethoxylated alcohols, preferably having an average degree of ethoxylation of from 1 to 7; C_{12} - C_{18} 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.

Suitable detersive surfactants include anionic detersive surfactants, nonionic detersive surfactants, cationic detersive surfactants, zwitterionic detersive surfactants, amphoteric detersive surfactants and mixtures thereof.

Suitable anionic detersive 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: C_{10} - C_{18} alkyl benzene sulphonates (LAS) preferably C_{10} - C_{13} alkyl benzene sulphonates; C_{10} - C_{20} primary, branched chain, linear-chain and random-chain alkyl sulphates (AS), typically having the following formula:

CH₃(CH₂)xCH₂-OSO₃⁻ M⁺

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; C_{10} - C_{18} secondary (2,3) alkyl sulphates, typically having the following formulae:

OSO₃ M⁺ CH₃(CH₂)_x(CH)CH₃ OSO₃ M⁺ CH₃(CH₂)_y(CH)CH₂CH₃

14

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.

Preferred anionic detersive surfactants include: linear or branched, substituted or unsubstituted alkyl benzene sulphonate detersive surfactants, preferably linear C₈-C₁₈ alkyl benzene sulphonate detersive surfactants; linear or branched, substituted or unsubstituted alkyl benzene sulphate detersive surfactants; linear or branched, substituted or unsubstituted alkyl sulphate detersive surfactants, including linear C₈-C₁₈ alkyl sulphate detersive surfactants, C₁-C₃ alkyl branched C₈-C₁₈ alkyl sulphate detersive surfactants, linear or branched alkoxylated C₈-C₁₈ alkyl sulphate detersive surfactants and mixtures thereof; linear or branched, substituted or unsubstituted alkyl sulphonate detersive surfactants; and mixtures thereof.

Preferred alkoxylated alkyl sulphate detersive surfactants are linear or branched, substituted or unsubstituted C₈₋₁₈ alkyl alkoxylated sulphate detersive surfactants having an average degree of alkoxylation of from 1 to 30, preferably from 1 to 10. Preferably, the alkoxylated alkyl sulphate detersive surfactant is a linear or branched, substituted or unsubstituted C₈₋₁₈ alkyl ethoxylated sulphate having an average degree of ethoxylation of from 1 to 10. Most preferably, the alkoxylated alkyl sulphate detersive surfactant is a linear unsubstituted C₈₋₁₈ alkyl ethoxylated sulphate having an average degree of ethoxylation of from 3 to 7.

Preferred anionic detersive surfactants are selected from the group consisting of: linear or branched, substituted or unsubstituted, C₁₂₋₁₈ alkyl sulphates; linear or branched, substituted or unsubstituted, C_{10-13} alkylbenzene sulphonates, preferably linear C_{10-13} alkylbenzene sulphonates; and mixtures thereof. Highly preferred are linear C₁₀₋₁₃ alkylbenzene sulphonates. Highly preferred are linear C_{10-13} alkylbenzene sulphonates that are obtainable, preferably obtained, by sulphonating commercially available linear alkyl benzenes (LAB); suitable LAB include low 2-

15

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 detersive surfactant is alkyl benzene sulphonate that is obtained by DETAL catalyzed process, although other synthesis routes, such as HF, may also be suitable.

Another suitable anionic detersive surfactant is alkyl ethoxy carboxylate. The anionic detersive surfactants are typically present in their salt form, typically being complexed with a suitable cation. Suitable counter-ions include Na^+ and K^+ , substituted ammonium such as C_1 - C_6 alkanolammnonium preferably mono-ethanolamine (MEA) triethanolamine (TEA), di-ethanolamine (DEA), and any mixtures thereof.

However, preferably at least 20wt%, or at least 30wt%, or at least 40wt%, or at least 50wt%, or at least 60wt%, or at least 70wt%, or at least 80wt%, or even or at least 90wt% of the anionic detersive surfactant is neutralized by a sodium cation.

Suitable cationic detersive surfactants include: alkyl pyridinium compounds; alkyl quaternary ammonium compounds; alkyl quaternary phosphonium compounds; alkyl ternary sulphonium compounds; and mixtures thereof. The cationic detersive surfactant can be selected from the group consisting of: alkoxylate 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 detersive surfactants are quaternary ammonium compounds having the general formula:

$(R)(R_1)(R_2)(R_3)N^+X^-$

wherein, R is a linear or branched, substituted or unsubstituted C_{6-18} alkyl or alkenyl moiety, R_1 and R_2 are independently selected from methyl or ethyl moieties, R_3 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 detersive surfactants are mono- C_{6-18} alkyl mono-hydroxyethyl di-methyl quaternary ammonium chlorides. Highly preferred cationic detersive surfactants are mono- C_{8-10} alkyl mono-hydroxyethyl di-methyl quaternary ammonium chloride, mono- C_{10-12} alkyl mono-hydroxyethyl

16

di-methyl quaternary ammonium chloride and mono- C_{10} alkyl mono-hydroxyethyl di-methyl quaternary ammonium chloride.

Suitable non-ionic detersive surfactant can be selected from the group consisting of: C_{8} - C_{18} alkyl ethoxylates, such as, NEODOL® non-ionic surfactants from Shell; C_6 - C_{12} alkyl phenol alkoxylates wherein the alkoxylate units are ethyleneoxy units, propyleneoxy units or a mixture thereof; C_{12} - C_{18} alcohol and C_6 - C_{12} alkyl phenol condensates with ethylene oxide/propylene oxide block polymers such as Pluronic® from BASF; C_{14} - C_{22} mid-chain branched alcohols, BA, as described in more detail in US 6,150,322; C_{14} - C_{22} mid-chain branched alkyl alkoxylates, 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.

The non-ionic detersive surfactant could be an alkyl polyglucoside and/or an alkyl alkoxylated alcohol. Preferably the non-ionic detersive surfactant is a linear or branched, substituted or unsubstituted C_{8-18} alkyl ethoxylated alcohol having an average degree of ethoxylation of from 1 to 10, more preferably from 3 to 7.

Suitable zwitterionic and/or amphoteric detersive surfactants include alkanolamine sulpho-betaines.

It may be preferred for the composition to comprise branched anionic detersive surfactant and/or branched non-ionic detersive surfactant. Preferably, the branched anionic detersive surfactant and/or branched non-ionic detersive surfactant are derived from natural sources, preferably wherein the natural sources include bio-derived isoprenoids, most preferably farnescene.

Surfactancy boosting polymer. The composition may comprise a surfactancy boosting polymer. Preferred polymers are amphiphilic alkoxylated grease cleaning polymers and/or random graft co-polymers. These polymers are described in more detail below.

Other polymers. The composition preferably comprises polymer. Suitable polymers include polyamines, preferably polyethylene imines, most preferably alkoxylated polyethylene imines. Other suitable polymers include dye transfer inhibitors, such as polyvinyl pyrrolidone polymer, polyamine N-oxide polymer, co-polymer of N-vinylpyrrolidone and N-vinylimidazole polymers.

PCT/US2010/041289

Non-polymeric dye transfer inhibitors. Non-polymeric dye transfer inhibitors may also be used, such as manganese phthalocyanine, peroxidases, and mixtures thereof.

Amphiphilic alkoxylated grease cleaning polymer. Amphiphilic alkoxylated grease cleaning polymers refer to any alkoxylated polymers having balanced hydrophilic and hydrophobic properties such that they remove grease particles from fabrics and surfaces. Specific embodiments of the amphiphilic alkoxylated grease cleaning polymers of the present invention comprise a core structure and a plurality of alkoxylate groups attached to that core structure.

The core structure may comprise a polyalkylenimine structure comprising, in condensed form, repeating units of formulae (I), (II), (III) and (IV):

wherein # in each case denotes one-half of a bond between a nitrogen atom and the free binding position of a group A¹ of two adjacent repeating units of formulae (I), (II), (III) or (IV); * in each case denotes one-half of a bond to one of the alkoxylate groups; and A¹ is independently selected from linear or branched C₂-C₆-alkylene; wherein the polyalkylenimine structure consists of 1 repeating unit of formula (I), x repeating units of formula (II), y repeating units of formula (III) and y+1 repeating units of formula (IV), wherein x and y in each case have a value in the range of from 0 to about 150; where the average weight average molecular weight, Mw, of the polyalkylenimine core structure is a value in the range of from about 60 to about 10,000 g/mol.

The core structure may alternatively comprise a polyalkanolamine structure of the condensation products of at least one compound selected from N-(hydroxyalkyl)amines of formulae (I.a) and/or (I.b),

18

wherein A are independently selected from C_1 - C_6 -alkylene; R^1 , R^1* , R^2 , R^2* , R^3 , R^3* , R^4 , R^4* , R^5 and R^5* are independently selected from hydrogen, alkyl, cycloalkyl or aryl, wherein the last three mentioned radicals may be optionally substituted; and R^6 is selected from hydrogen, alkyl, cycloalkyl or aryl, wherein the last three mentioned radicals may be optionally substituted.

The plurality of alkylenoxy groups attached to the core structure are independently selected from alkylenoxy units of the formula (V)

$$* - A^2 O - \frac{1}{m} - CH_2 - CH_2 - O - \frac{3}{n} - A^3 O - \frac{1}{p} - R$$

(V)

wherein * in each case denotes one-half of a bond to the nitrogen atom of the repeating unit of formula (I), (II) or (IV); A^2 is in each case independently selected from 1,2-propylene, 1,2-butylene and 1,2-isobutylene; A^3 is 1,2-propylene; R is in each case independently selected from hydrogen and C_1 - C_4 -alkyl; m has an average value in the range of from 0 to about 2; n has an average value in the range of from about 20 to about 50; and p has an average value in the range of from about 10 to about 50.

Specific embodiments of the amphiphilic alkoxylated grease cleaning polymers may be selected from alkoxylated polyalkylenimines having an inner polyethylene oxide block and an outer polypropylene oxide block, the degree of ethoxylation and the degree of propoxylation not going above or below specific limiting values. Specific embodiments of the alkoxylated polyalkylenimines according to the present invention have a minimum ratio of polyethylene blocks to polypropylene blocks (n/p) of about 0.6 and a maximum of about $1.5(x+2y+1)^{1/2}$. Alkoxykated polyalkyenimines having an n/p ratio of from about 0.8 to about $1.2(x+2y+1)^{1/2}$ have been found to have especially beneficial properties.

The alkoxylated polyalkylenimines according to the present invention have a backbone which consists of primary, secondary and tertiary amine nitrogen atoms which are attached to one another by alkylene radicals A and are randomly arranged. Primary amino moieties which start or terminate the main chain and the side chains of the polyalkylenimine backbone and whose remaining hydrogen atoms are subsequently replaced by alkylenoxy units are referred to as repeating units of formulae (I) or (IV), respectively. Secondary amino moieties whose remaining hydrogen atom is subsequently replaced by alkylenoxy units are referred to as repeating units of formula (II). Tertiary amino moieties which branch the main chain and the side chains are referred to as repeating units of formula (III).

19

Since cyclization can occur in the formation of the polyalkylenimine backbone, it is also possible for cyclic amino moieties to be present to a small extent in the backbone. Such polyalkylenimines containing cyclic amino moieties are of course alkoxylated in the same way as those consisting of the noncyclic primary and secondary amino moieties.

The polyalkylenimine backbone consisting of the nitrogen atoms and the groups A¹, has an average molecular weight Mw of from about 60 to about 10,000 g/mole, preferably from about 100 to about 8,000 g/mole and more preferably from about 500 to about 6,000 g/mole.

The sum (x+2y+1) corresponds to the total number of alkylenimine units present in one individual polyalkylenimine backbone and thus is directly related to the molecular weight of the polyalkylenimine backbone. The values given in the specification however relate to the number average of all polyalkylenimines present in the mixture. The sum (x+2y+2) corresponds to the total number amino groups present in one individual polyalkylenimine backbone.

The radicals A^1 connecting the amino nitrogen atoms may be identical or different, linear or branched C_2 - C_6 -alkylene radicals, such as 1,2-ethylene, 1,2-propylene, 1,2-butylene, 1,2-isobutylene,1,2-pentanediyl, 1,2-hexanediyl or hexamethylen. A preferred branched alkylene is 1,2-propylene. Preferred linear alkylene are ethylene and hexamethylene. A more preferred alkylene is 1,2-ethylene.

The hydrogen atoms of the primary and secondary amino groups of the polyalkylenimine backbone are replaced by alkylenoxy units of the formula (V).

*
$$-\left[-A^{2}O^{-}\right]_{m}\left[-CH_{2}^{-}CH_{2}^{-}O^{-}\right]_{n}\left[-A^{3}O^{-}\right]_{p}$$
R
(V)

In this formula, the variables preferably have one of the meanings given below:

 A^2 in each case is selected from 1,2-propylene, 1,2-butylene and 1,2-isobutylene; preferably A^2 is 1,2-propylene. A^3 is 1,2-propylene; R in each case is selected from hydrogen and C_1 - C_4 -alkyl, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl and tert.-butyl; preferably R is hydrogen. The index m in each case has a value of 0 to about 2; preferably m is 0 or approximately 1; more preferably m is 0. The index n has an average value in the range of from about 20 to about 50, preferably in the range of from about 22 to about 40, and more preferably in the range of from about 10 to about 50, preferably in the range of from about 11 to about 40, and more preferably in the range of from about 12 to about 30.

Preferably the alkylenoxy unit of formula (V) is a non-random sequence of alkoxylate blocks. By non-random sequence it is meant that the $[-A^2-O-]_m$ is added first (i.e., closest to the bond to the nitrgen atom of the repeating unit of formula (I), (II), or (III)), the $[-CH_2-CH_2-O-]_n$ is added second, and the $[-A^3-O-]_p$ is added third. This orientation provides the alkoxylated polyalkylenimine with an inner polyethylene oxide block and an outer polypropylene oxide block.

This initial modification of the polyalkylenimine backbone allows, if necessary, the viscosity of the reaction mixture in the alkoxylation to be lowered. However, the modification generally does not influence the performance properties of the alkoxylated polyalkylenimine and therefore does not constitute a preferred measure.

The amphiphilic alkoxylated grease cleaning polymers are present in the detergent and cleaning compositions of the present invention at levels ranging from about 0.05% to 10% by weight of the composition. Embodiments of the compositions may comprise from about 0.1% to about 5% by weight. More specifically, the embodiments may comprise from about 0.25 to about 2.5% of the grease cleaning polymer.

Random graft co-polymer. Suitable random graft co-polymers typically comprise: (i) hydrophilic backbone comprising monomers selected from the group consisting of: unsaturated $C_1.C_6$ carboxylic acids, ethers, alcohols, aldehydes, ketones, esters, sugar units, alkoxy units, maleic anhydride, saturated polyalcohols such as glycerol, and mixtures thereof; and (ii) hydrophobic side chain(s) selected from the group consisting of: $C_4.C_{25}$ alkyl group, polypropylene, polybutylene, vinyl ester of a saturated $C_1.C_6$ mono-carboxylic acid, $C_1.C_6$ alkyl ester of acrylic or methacrylic acid, and mixtures thereof.

The polymer preferably has the general formula:

wherein X, Y and Z are capping units independently selected from H or a C_{1-6} alkyl; each R^1 is independently selected from methyl and ethyl; each R^2 is independently selected from H and methyl; each R^3 is independently a C_{1-4} alkyl; and each R^4 is independently selected from pyrrolidone and phenyl groups. The weight average molecular weight of the polyethylene oxide backbone is typically from about 1,000 g/mol to about 18,000 g/mol, or from about 3,000 g/mol to about 13,500 g/mol, or from about 4,000 g/mol to about 9,000 g/mol. The value of m, n, o, p and q is selected such that the pendant groups comprise, by weight of the polymer at least 50%, or from about 50% to about 98%, or from about 55% to about 95%, or from about 60% to about 90%. The polymer useful herein typically has a weight average molecular weight of from about 1,000 to about 100,000 g/mol, or preferably from about 2,500 g/mol to about 45,000 g/mol, or from about 7,500 g/mol to about 33,800 g/mol, or from about 10,000 g/mol to about 22,500 g/mol.

Soil release polymers. Suitable soil release polymers include polymers comprising at least one monomer unit selected from saccharide, dicarboxylic acid, polyol and combinations thereof, in random or block configuration. Other suitable soil release polymers include ethylene terephthalate-based polymers and co-polymers thereof, preferably co-polymers of ethylene terephthalate and polyethylene oxide in random or block configuration.

Anti-redeposition polymers. The composition may comprise anti-redeposition polymer, preferably from 0.1wt% to 10wt% anti-redeposition polymer. Suitable anti-redeposition polymers include carboxylate polymers, such as polymers comprising at least one monomer

22

selected from acrylic acid, maleic acid (or maleic anhydride), fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid, methylenemalonic acid, and any mixture thereof. Suitable carboxylate polymers include.

Other suitable anti-redeposition polymers include polyethylene glycol, preferably having a molecular weight in the range of from 500 to 100,000 Da.

Carboxylate polymers. It may be preferred for the composition to comprise from above 0wt% to 5wt%, 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.

The composition preferably comprises polymeric carboxylate. 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.

Deposition aids. The composition may comprise deposition aid. Suitable deposition aids are polysaccharides, preferably cellulosic polymers. Other suitable deposition aids include poly diallyl dimethyl ammonium halides (DADMAC), and co-polymers of DADMAC with vinyl pyrrolidone, acrylamides, imidazoles, imidazolinium halides, and mixtures thereof, in random or block configuration. Other suitable deposition aids include cationic guar gum, cationic cellulose such as cationic hydoxyethyl cellulose, cationic starch, cationic polyacylamides, and mixtures thereof.

Chelant. Chelant may be but are not limited to the following: ethylene-diamine-tetraacetic acid (EDTA); diethylene triamine penta methylene phosphonic acid (DTPMP); hydroxy-ethane diphosphonic acid (HEDP); ethylenediamine N,N'-disuccinic acid (EDDS); methyl glycine diacetic acid (MGDA); diethylene triamine penta acetic acid (DTPA); propylene diamine tetracetic acid (PDTA); 2-hydroxypyridine-N-oxide (HPNO); or methyl glycine diacetic acid (MGDA); glutamic acid N,N-diacetic acid (N,N-dicarboxymethyl glutamic acid tetrasodium salt (GLDA); nitrilotriacetic acid (NTA); 4,5-dihydroxy-m-benzenedisulfonic acid; citric acid; and any salts thereof.

23

The chelant are typically present at a level of from 0.1wt% to 10wt% by weight in the composition. The chelant may be in form of a solid particle that is suspended in the liquid composition.

Hueing dyes. The composition may comprise hueing dye. Hueing dyes are formulated to deposit onto fabrics from the wash liquor so as to improve fabric whiteness perception. Preferably the hueing agent dye is blue or violet. It is preferred that the shading dye(s) have a peak absorption wavelength of from 550nm to 650nm, preferably from 570nm to 630nm. A combination of dyes which together have the visual effect on the human eye as a single dye having a peak absorption wavelength on polyester of from 550nm to 650nm, preferably from 570nm to 630nm. This may be provided for example by mixing a red and green-blue dye to yield a blue or violet shade.

Dyes are coloured organic molecules which are soluble in aqueous media that contain surfactants. Dyes are described in 'Industrial Dyes', Wiley VCH 2002, K. Hunger (editor). Dyes are listed in the Color Index International published by Society of Dyers and Colourists and the American Association of Textile Chemists and Colorists. Dyes are preferably selected from the classes of basic, acid, hydrophobic, direct and polymeric dyes, and dye-conjugates. Those skilled in the art of detergent formulation are able to select suitable hueing dyes from these publications. Polymeric hueing dyes are commercially available, for example from Milliken, Spartanburg, South Carolina, USA.

Examples of suitable dyes are direct violet 7, direct violet 9, direct violet 11, direct violet 26, direct violet 31, direct violet 35, direct violet 40, direct violet 41, direct violet 51, direct violet 66, direct violet 99, acid violet 50, acid blue 9, acid violet 17, acid black 1, acid red 17, acid blue 29, solvent violet 13, disperse violet 27 disperse violet 26, disperse violet 28, disperse violet 63 and disperse violet 77, basic blue 16, basic blue 65, basic blue 66, basic blue 67, basic blue 71, basic blue 159, basic violet 19, basic violet 35, basic violet 38, basic violet 48; basic blue 3, basic blue 75, basic blue 95, basic blue 122, basic blue 124, basic blue 141, thiazolium dyes, reactive blue 19, reactive blue 163, reactive blue 182, reactive blue 96, Liquitint® Violet CT (Milliken, Spartanburg, USA) and Azo-CM-Cellulose (Megazyme, Bray, Republic of Ireland).

Enzymes. The composition prefereably comprises enzyme. Preferably, the composition comprises a relatively high level of enzymes. Most preferably, the composition comprises at least 0.01wt% active enzyme. It may be preferred for the composition to comprise at least 0.03wt% active enzyme.

It may be preferred for the composition to comprise at least a ternary enzyme system selected from protease, amylase, lipase and/or cellulase.

Lipase. Suitable lipases include those of bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Examples of useful lipases include lipases from *Humicola* (synonym *Thermomyces*), e.g., from *H. lanuginosa* (*T. lanuginosus*) as described in EP 258 068 and EP 305 216 or from *H. insolens* as described in WO 96/13580, a Pseudomonas lipase, e.g., from *P. alcaligenes* or *P. pseudoalcaligenes* (EP 218 272), *P. cepacia* (EP 331 376), *P. stutzeri* (GB 1,372,034), *P. fluorescens, Pseudomonas* sp. strain SD 705 (WO 95/06720 and WO 96/27002), *P. wisconsinensis* (WO 96/12012), a *Bacillus* lipase, e.g., from *B. subtilis* (Dartois et al. (1993), Biochemica et Biophysica Acta, 1131, 253-360), *B. stearothermophilus* (JP 64/744992) or *B. pumilus* (WO 91/16422).

The lipase may be a "first cycle lipase" such as those described in U.S. Patent 6,939,702 and US PA 2009/0217464. In one aspect, the lipase is a first-wash lipase, preferably a variant of the wild-type lipase from Thermomyces lanuginosus comprising T231R and N233R mutations. The wild-type sequence is the 269 amino acids (amino acids 23 – 291) of the Swissprot accession number Swiss-Prot O59952 (derived from Thermomyces lanuginosus (Humicola lanuginosa)). Preferred lipases would include those sold under the tradenames Lipex®, Lipolex® and Lipoclean® by Novozymes, Bagsvaerd, Denmark.

Preferably, the composition comprises a variant of Thermomyces lanuginosa lipase having >90% identity with the wild type amino acid and comprising substitution(s) at T231 and/or N233, preferably T231R and/or N233R (herein: "first wash lipase").

Protease. Suitable proteases include metalloproteases and/or serine proteases, including neutral or alkaline microbial serine proteases, such as subtilisins (EC 3.4.21.62). Suitable proteases include those of animal, vegetable or microbial origin. In one aspect, such suitable protease may be of microbial origin. The suitable proteases include chemically or genetically modified mutants of the aforementioned suitable proteases. In one aspect, the suitable protease may be a serine protease, such as an alkaline microbial protease or/and a trypsin-type protease. Examples of suitable neutral or alkaline proteases include:

- (a) subtilisins (EC 3.4.21.62), including those derived from Bacillus, such as Bacillus lentus, B. alkalophilus, B. subtilis, B. amyloliquefaciens, Bacillus pumilus and Bacillus gibsonii described in US 6,312,936, US 5,679,630, US 4,760,025, US 7,262,042 and WO09/021867.
- (b) trypsin-type or chymotrypsin-type proteases, such as trypsin (e.g., of porcine or bovine origin), including the Fusarium protease described in WO 89/06270 and the chymotrypsin proteases derived from Cellumonas described in WO 05/052161 and WO 05/052146.
- (c) metalloproteases, including those derived from Bacillus amyloliquefaciens described in WO 07/044993.

Preferred proteases include those derived from Bacillus gibsonii or Bacillus Lentus. Suitable commercially available protease enzymes include those sold under the trade names Alcalase®, Savinase®, Primase®, Durazym®, Polarzyme®, Kannase®, Liquanase®, Liquanase®, Liquanase Ultra®, Savinase Ultra®, 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, those sold under the tradename Opticlean® and Optimase® by Solvay Enzymes, those available from Henkel/ Kemira, namely BLAP (sequence shown in Figure 29 of US 5,352,604 with the folowing mutations S99D + S101 R + S103A + V104I + G159S, hereinafter referred to as BLAP), BLAP R (BLAP with S3T + V4I + V199M + V205I + L217D), BLAP X (BLAP with S3T + V4I + V205I) and BLAP F49 (BLAP with S3T + V4I + A194P + V199M + V205I + L217D) - all from Henkel/Kemira; and KAP (Bacillus alkalophilus subtilisin with mutations A230V + S256G + S259N) from Kao.

Preferably, the composition comprises a subtilisin protease selected from BLAP, BLAP R, BLAP X or BLAP F49.

Cellulase. Suitable cellulases include those of bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Suitable cellulases include cellulases from the genera *Bacillus, Pseudomonas, Humicola, Fusarium, Thielavia, Acremonium*, e.g., the fungal cellulases produced from *Humicola insolens, Myceliophthora thermophila* and *Fusarium oxysporum* disclosed in US 4,435,307, US 5,648,263, US 5,691,178, US 5,776,757 and WO 89/09259.

In one aspect, the cellulase can include microbial-derived endoglucanases exhibiting endo-beta-1,4-glucanase activity (E.C. 3.2.1.4), including a bacterial polypeptide endogenous to a member of the genus Bacillus which has a sequence of at least 90%, 94%, 97% and even 99% identity to the amino acid sequence SEQ ID NO:2 in US 7,141,403 and mixtures thereof. A suitable endoglucanases is sold under the tradename Celluclean® (Novozymes A/S, Bagsvaerd, Denmark). Further suitable endoglucanases are variants of the XYG1006 enzyme described in US 7,361,736 (Novozymes). A suitable endoglucanase is sold under the tradename Whitezyme® (Novozymes A/S, Bagsvaerd, Denmark).

Preferably, the composition comprises a cleaning cellulase belonging to Glycosyl Hydrolase family 45 having a molecular weight of from 17kDa to 30 kDa, for example the endoglucanases sold under the tradename Biotouch® NCD, DCC and DCL (AB Enzymes, Darmstadt, Germany).

Amylase. Preferably, the composition comprises an amylase with greater than 60% identity to the AA560 alpha amylase endogenous to Bacillus sp. DSM 12649, preferably a variant of the AA560 alpha amylase endogenous to Bacillus sp. DSM 12649 having:

(a) mutations at one or more of positions 9, 26, 149. 182, 186, 202, 257, 295, 299, 323, 339 and 345; and

(b) optionally with one or more, preferably all of the substitutions and/or deletions in the following positions: 118, 183, 184, 195, 320 and 458, which if present preferably comprise R118K, D183*, G184*, N195F, R320K and/or R458K.

Suitable commercially available amylase enzymes include Stainzyme® Plus, Stainzyme®, Natalase, Termamyl®, Termamyl® Ultra, Liquezyme® SZ (all Novozymes, Bagsvaerd, Denmark) and Spezyme® AA or Ultraphlow (Genencor, Palo Alto, USA).

Choline oxidase. Preferably, the composition comprises a choline oxidase enzyme such as the 59.1 kDa choline oxidase enzyme endogenous to *Arthrobacter nicotianae*, produced using the techniques disclosed in D. Ribitsch *et al.*, Applied Microbiology and Biotechnology, Volume 81, Number 5, pp875-886, (2009).

Other enzymes. Other suitable enzymes are peroxidases/oxidases, which include those of plant, bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Examples of useful peroxidases include peroxidases from Coprinus, e.g., from *C. cinereus*, and variants thereof as those described in WO 93/24618, WO 95/10602, and WO 98/15257.

Commercially available peroxidases include GUARDZYME® (Novozymes A/S).

Other preferred enzymes include: pectate lyases sold under the tradenames Pectawash®, Pectaway®; mannanases sold under the tradenames Mannaway® (all from Novozymes A/S, Bagsvaerd, Denmark), and Purabrite® (Genencor International Inc., Palo Alto, California); cutinases; phospholipases; and any mixture thereof.

Identity. The relativity between two amino acid sequences is described by the parameter "identity". For purposes of the present invention, the alignment of two amino acid sequences is determined by using the Needle program from the EMBOSS package (http://emboss.org) version 2.8.0. The Needle program implements the global alignment algorithm described in Needleman, S. B. and Wunsch, C. D. (1970) J. Mol. Biol. 48, 443-453. The substitution matrix used is BLOSUM62, gap opening penalty is 10, and gap extension penalty is 0.5.

Enzyme stabilizer. The composition may comprise an enzyme stabilizer. Suitable enzyme stabilizers include polyols such as propylene glycol or glycerol, sugar or sugar alcohol, lactic acid, reversible protease inhibitor, boric acid, or a boric acid derivative, e.g., an aromatic borate ester, or a phenyl boronic acid derivative such as 4-formylphenyl boronic acid. It may be

preferred for the composition to comprise a nil-boron enzyme stabilizer, preferably selected from polyols such as propylene glycol or glycerol, sugar or sugar alcohol. It may even be preferred for the composition to be substantially free of boron. By substantially free it is typically meant: "comprises no deliberately added".

Calcium and Magnesium cations. Preferably, the composition comprises from at least 0.2wt% to 5wt% calcium and/or magnesium cations.

Visual signaling ingredients. Suitable visual signaling ingredients include any reflective and/or refractive material, preferably mica.

Structurant. The composition may comprise a structurant selected from the group consisting of diglycerides and triglycerides, ethylene glycol distearate microcrystalline cellulose, cellulose-based materials, microfiber cellulose, biopolymers, xanthan gum, gellan gum, and mixtures thereof. A suitable structurant includes castor oil and its derivatives such as hydrogenated castor oil.

Solvent. The composition preferably comprises solvent. Preferred solvents include alcohols and/or glycols, preferably methanol, ethanol and/or propylene glycol. Preferably, the composition comprises no or minimal amounts of methanol and ethanol and instead comprises relatively high amounts of propylene glycol, for improved enzyme stability. Preferably, the composition comprises propylene glycol.

Suitable solvents include C_4 - C_{14} ethers and diethers, glycols, alkoxylated glycols, C_6 - C_{16} glycol ethers, alkoxylated aromatic alcohols, aromatic alcohols, aliphatic branched alcohols, alkoxylated linear C_1 - C_5 alcohols, linear C_1 - C_5 alcohols, amines, C_8 - C_{14} alkyl and cycloalkyl hydrocarbons and halohydrocarbons, and mixtures thereof.

Preferred solvents are selected from methoxy octadecanol, 2-(2-ethoxyethoxy)ethanol, benzyl alcohol, 2-ethylbutanol and/or 2- methylbutanol, 1-methylpropoxyethanol and/or 2- methylbutoxyethanol, linear C₁-C₅ alcohols such as methanol, ethanol, propanol, butyl diglycol ether (BDGE), butyltriglycol ether, tert-amyl alcohol, glycerol, isopropanol and mixtures thereof. Particularly preferred solvents which can be used herein are butoxy propoxy propanol, butyl diglycol ether, benzyl alcohol, butoxypropanol, propylene glycol, glycerol, ethanol, methanol, isopropanol and mixtures thereof. Other suitable solvents include propylene glycol and diethylene glycol and mixtures thereof.

Buffers. The composition typically comprises buffer. Preferred buffers include monoethanolamine (MEA) and tri-ethanolamine (TEA). Borax may be used as a buffer, although preferably the composition is substantially free of borax, by substantially free it is typically meant no deliberately added borax is incorporated into the composition.

Alkanolammonium cation. Preferably, the composition comprises alkanolammonium cation, preferably mono-ethanolamine (MEA) and/or tri-ethanolamine (TEA).

Hydrotropes. The composition may comprise hydrotrope. A preferred hydrotrope is monopropylene glycol.

Zeolite builder. 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. 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. 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.

Other detergent ingredients. The composition typically comprises other detergent ingredients. Suitable detergent ingredients include: imine bleach catalysts such as sulphuric acid mono-[2-(3,4-dihydro-isoquinolin-2-yl)-1-(2-butyl-octyloxymethyl)-ethyl] ester, internal salt; 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; fabricsoftening agents such as clay, silicone and/or quaternary ammonium compounds; flocculants such as polyethylene oxide; dye transfer inhibitors such as polyvinylpyrrolidone, poly 4vinylpyridine N-oxide and/or co-polymer of vinylpyrrolidone and vinylimidazole; fabric integrity components such as oligomers produced by the condensation of imidazole and epichlorhydrin; 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 and sodium metasilicate; co-polyesters of di-carboxylic acids and diols; cellulosic polymers such as methyl cellulose, carboxymethyl cellulose, hydroxyethoxycelluloase, or other alkyl or alkylalkoxy cellulose; and any combination thereof.

Free water. The composition preferably comprises less than 10wt%, or less than 5wt%, or less than 4wt% or less than 3wt% free water, or less than 2wt% free water, or less than 1wt% free water, and may even be anhydrous, typically comprising no deliberately added free water. Free water is typically measured using Karl Fischer titration. 2g of the laundry detergent composition is extracted into 50ml dry methanol at room temperature for 20 minutes and analyse 1ml of the methanol by Karl Fischer titration.

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

Every document cited herein, including any cross referenced or related patent or application, is hereby incorporated herein by reference in its entirety unless expressly excluded or otherwise limited. The citation of any document is not an admission that it is prior art with respect to any invention disclosed or claimed herein or that it alone, or in any combination with any other reference or references, teaches, suggests or discloses any such invention. Further, to the extent that any meaning or definition of a term in this document conflicts with any meaning or definition of the same term in a document incorporated by reference, the meaning or definition assigned to that term in this document shall govern.

While particular embodiments of the present invention have been illustrated and described, it would be obvious to those skilled in the art that various other changes and modifications can be made without departing from the spirit and scope of the invention. It is therefore intended to cover in the appended claims all such changes and modifications that are within the scope of this invention.

EXAMPLES

Example 1: Method of laundering with a laundry detergent composition

15g of the following liquid 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), 15°C wash temperature).

Example	A	В	C	D	E
Ingredient	Wt%	Wt%	Wt%	Wt%	Wt%

The following ingredients are in					
the form of a continuous liquid					
phase					
Sodium alkyl ether sulfate	20.5	22	18	26	29.7
Branched alcohol sulfate	5.8	4.8	6.4	8.4	7.7
Linear Alkylbenzene Sulfonic	2.5	2.5	2.1	6.1	8.4
Acid	0.0	1.1	1 /	2.4	1 /
Alkyl ethoxylate	0.8		1.4	2.4	1.4
C12-14 Amine oxide	0.2	0.2	1.0	1.1	
Citric Acid		1.0	1.2	0.4	
C12-18 Fatty Acid	0.7	1.0	0.9		
Protease	0.7			0.6	0.6
Amylase	0.4			0.4	
Borax	3.0			2.2	
Calcium and Sodium formate	0.22	0.31	0.22	0.35	
Amine Ethoxylate Polymers	1.2	1.0		1.2	
Zwitterionic Amine Ethoxylate Polymers	1.0	1.5		3.1	
Diethylene Triamine Penta Acetic Acid (DTPA)	0.35	0.25	0.61	0.44	0.41
Fluorescent whitening agent(s)	0.2	0.3	0.3	0.3	
Ethanol	2.9	3.9	2.0	1.6	4.3
Propane diol	5.0	4.0	2.0	3.1	6.5
Diethylene glycol (DEG)	2.6	3.6	4.6	4.7	4.9
Poly ethylene glycol 4000	0.15				
Monoethanolamine (MEA)	2.7	3.7	5.1	5.1	
Sodium hydroxide (NaOH)	3.8	1.2	2.0		3.1
Sodium Cumene Sulfonate		0.08			
Silicone Suds Suppressor	0.11	0.10			0.06
Perfume	0.5	0.3	1.2		0.8
Perfume microcapsules	0.4			0.9	
Formaldehyde scavenger	0.1			0.2	
Hueing agent and dyes	0.11	0.13	0.0.8	0.10	
The following ingredients are in					
the form of a discontinuous					
solid particulate phase					
suspended within the					
continuous liquid phase					
6-(Phthalimidoperoxy)hexanoic acid (PAP)	1.0	1.2	1.0	2.1	3.0
Metal catalyst			0.05		
[Mn(Bcyclam*)Cl ₂]			0.05		
Sulphuric acid mono-[2-(3,4-					
dihydro-isoquinolin-2-yl)-1-(2-		0.05		0.16	
butyl-octyloxymethyl)-ethyl]		0.03		0.10	
ester, internal salt					
N-methyl-3,4-					
dihydroisoquinolinium	0.09				0.14
tetrafluoroborate					

31

Sodium percarbonate	4					
Sodium						
nonanoyloxybenzenesulfonate	1.4					
(NOBS)						
Tetraacetylethylenediamine	1.3					
(TAED)	1.3			I		
Sodium carbonate	1.5					
Citric Acid	3.5	3.7	0.5	4.5		
C12-18 Fatty Acid (excluding	2.0	3.0	4.2	1.5	6.2	
palmitic acid)	2.0	3.0	4.2	1.3	0.2	
Palmitic acid (hexadecanoic acid)	2.5	0.5		4.4		
Sodium bisulfate			2.4		2.1	
Water	balance	balance	balance	balance	balance	

^{* &}quot;Bcylcam" = 5,12-diethyl-1,5,8,12-tetraazo-bicyclo[6.6.2]hexadecane

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

32

CLAIMS

What is claimed is:

1. A method of laundering fabric comprising the step of contacting a liquid laundry detergent composition comprising a pre-formed peracid to water to form a wash liquor, and laundering fabric in said wash liquor,

wherein the laundry detergent is contacted to water in such an amount so that the concentration of laundry detergent composition in the wash liquor is from above 0g/l to 4g/l, and wherein from 0.01kg to 2kg of fabric per litre of wash liquor is dosed into said wash liquor.

- 2. A method according to claim 1, wherein the pre-formed peracid is in encapsulated form.
- 3. A method according to any preceding claim, wherein the pre-formed peracid is selected from peroxycarboxylic acid, salts thereof, peroxysulphonic acid, salts thereof, or mixtures thereof.
- 4. A method according to any preceding claim, wherein the composition comprises a bleach catalyst having a structure corresponding to general formula below:

$$OSO_3^{\Theta} O - R^{13}$$

wherein R^{13} is a branched alkyl group containing from three to 24 carbon atoms (including the branching carbon atoms) or a linear alkyl group containing from one to 24 carbon atoms.

- 5. A method according to any preceding claim, wherein the composition is essentially free of a source of hydrogen peroxide.
- 6. A method according to any preceding claim, wherein the composition comprises:
 - (a) detersive surfactant;
 - (b) pre-formed peracid;
 - (c) optionally bleach catalyst;
 - (d) from 0wt% to 4wt% source of hydrogen peroxide;
 - (e) from 0wt% to 10wt% zeolite builder;

33

- (f) from 0wt% to 10wt% phosphate builder
- (g) from 0wt% to less than 10wt% fatty acid;
- (h) from 0wt% to less than 5wt% source of boron;
- (i) optionally, an amine neutralized detersive surfactant; and
- (j) optionally other detergent ingredients.
- 7. A method according to any preceding claim, wherein 25g or less of laundry detergent composition is contacted to water to form the wash liquor.
- 8. A method according to any preceding claim, wherein the laundry detergent composition is contacted to 15 litres or less of water to form the wash liquor.
- 9. A method according to any preceding claim, wherein the laundry detergent is contacted to water in such an amount so that the concentration of laundry detergent composition in the wash liquor is from 1g/l to 3g/l.
- 10. A method according to any preceding claim, wherein at least 0.2kg fabric per litre of wash liquor is dosed into said wash liquor.
- 11. A method according to any preceding claim, wherein the method is carried out using a front-loading automatic washing machine.
- 12. A liquid laundry detergent composition suitable for use in the method according to any preceding claim, wherein the composition comprises:
 - (a) detersive surfactant;
 - (b) pre-formed peracid;
 - (c) optionally bleach catalyst;
 - (d) from 0wt% to 4wt% source of hydrogen peroxide;
 - (e) from 0wt% to 10wt% zeolite builder;
 - (f) from 0wt% to 10wt% phosphate builder
 - (g) from 0wt% to less than 10wt% fatty acid;
 - (h) from 0wt% to less than 5wt% source of boron;
 - (i) optionally, an amine neutralized detersive surfactant; and
 - (j) optionally other detergent ingredients.

INTERNATIONAL SEARCH REPORT

International application No PCT/US2010/041289

A. CLASSIFICATION OF SUBJECT MATTER INV. C11D3/39 C11D3 C11D3/395 C11D17/00 ADD. According to International Patent Classification (IPC) or to both national classification and IPC **B. FIELDS SEARCHED** Minimum documentation searched (classification system followed by classification symbols) C11D Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data C. DOCUMENTS CONSIDERED TO BE RELEVANT Category* Citation of document, with indication, where appropriate, of the relevant passages Relevant to claim No. χ US 2001/044401 A1 (PERKINS CHRISTOPHER 1-12 MARK [US] ET AL) 22 November 2001 (2001-11-22) paragraphs [0002], [0350] - [0356], [0404], [0561] - [0565], [0601] - [0603]; claims [0403], [0593], 1-39,42-44; examples 6,10,11 X WO 2007/077088 A1 (HENKEL KGAA [DE]; 1-12 SCHMIEDEL PETER [DE]; BELLOMI LUCA [DE]; RYBINSKI WO) 12 July 2007 (2007-07-12) page 1, paragraphs 1,2; claims 1-10; example 1 -/--Х Further documents are listed in the continuation of Box C. See patent family annex. Special categories of cited documents: *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the *A* document defining the general state of the art which is not considered to be of particular relevance invention *E* earlier document but published on or after the international *X* document of particular relevance; the claimed invention filing date cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such docu-*O* document referring to an oral disclosure, use, exhibition or ments, such combination being obvious to a person skilled other means *P* document published prior to the international filing date but later than the priority date claimed '&' document member of the same patent family Date of the actual completion of the international search Date of mailing of the international search report 7 October 2010 27/10/2010 Name and mailing address of the ISA/ Authorized officer European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040. Klier, Erich Fax: (+31-70) 340-3016

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2010/041289

		PCT/US2010/041289		
	tion). DOCUMENTS CONSIDERED TO BE RELEVANT			
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.		
X	WO 2008/122478 A1 (HENKEL AG & CO KGAA [DE]; SCHMIEDEL PETER [DE]; SCHOLL ELKE [DE]; RYBI) 16 October 2008 (2008-10-16) page 5, paragraph 2 - page 6, paragraph 1; claims 1-15; example 1	1-12		
X	EP 1 065 263 A1 (PROCTER & GAMBLE [US]) 3 January 2001 (2001-01-03) paragraphs [0001], [0004], [0117], [0119], [0121], [0122]; claims 1-13; examples I-VI	1-12		
X	US 5 441 660 A (TSAUR LIANG S [US] ET AL) 15 August 1995 (1995-08-15) column 2, line 66 - column 3, line 3; claims 1,3,6,9,13; examples 2,12-14; tables 5,6	1-12		
X	EP 1 811 014 A1 (PROCTER & GAMBLE [US]) 25 July 2007 (2007-07-25) paragraphs [0001], [0012], [0016], [2548]; claims 1-20	1-12		

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2010/041289

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
US 2001044401	A1	22-11-2001	US	6306812	B1	23-10-2001
WO 2007077088	A1	12-07-2007	DE EP JP	102005063180 1979453 2009522386	A1	05-07-2007 15-10-2008 11-06-2009
WO 2008122478	A1	16-10-2008	EP JP US	2132288 2010523748 2010081603	T	16-12-2009 15-07-2010 01-04-2010
EP 1065263	A1	03-01-2001	AU BR CA JP MX WO	5772800 0012102 2377350 2003503584 PA02000055 0100772	A A1 T A	31-01-2001 02-04-2002 04-01-2001 28-01-2003 02-07-2002 04-01-2001
US 5441660	Α	15 - 08-1995	NON	<i></i> NE		·
EP 1811014	A1	25-07-2007	AT CA CN WO JP US ZA	465230 2633695 101370922 2007083276 2009523853 2007173428 200805717	A1 A1 T A1	15-05-2010 26-07-2007 18-02-2009 26-07-2007 25-06-2009 26-07-2007 25-11-2009