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(71) Applicant (for all designated States except US): **THE PROCTER & GAMBLE COMPANY** [US/US]; One Procter & Gamble Plaza, Cincinnati, Ohio 45202 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **DE POORTERE, Johan, Maurice Theo** [BE/BE]; Campagnestraat 14, B-9820 Merelbeke (BE). **DYKSTRA, Robert, Richard** [US/US]; 7715 Mitchell Park Drive, Cleves, Ohio 45002 (US). **LABEQUE, Regine** [FR/BE]; Rue de Lombardzide 27/7, B-1120 Neder-over-Heembeek, Brussels (BE). **DITULLIO, Daniel, Dale, Jr.** [US/US]; 7004 Huntersmoon Court, Hamilton, Ohio 45011 (US).

(74) Common Representative: **THE PROCTER & GAMBLE COMPANY**; c/o Eileen L. Hughett, Global Patent

Services, 299 East Sixth Street, Sycamore Building, 4th Floor, Cincinnati, Ohio 45202 (US).

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(54) Title: OPTIMIZED RELEASE OF BLEACHING SYSTEMS IN LAUNDRY DETERGENTS

(57) Abstract: The need for a stable, safe on fabric, bleaching laundry detergent, that is also convenient to use, can be met by incorporating an aryliminium cation and/or zwitterion, and an activated peroxygen source, into fluid portions of a unit dose laundry detergent article. Such unit dose articles also result in reduced damage from bleach spotting.



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OPTIMIZED RELEASE OF BLEACHING SYSTEMS IN LAUNDRY DETERGENTS

FIELD OF THE INVENTION

- 5 The present invention relates to stable, convenient to use, unit dose laundry detergent articles that are capable of delivering good cleaning, including bleaching, while also being safe for fabrics.

BACKGROUND OF THE INVENTION

- 10 Today's consumer desires a laundry product with improved cleaning efficiency while being convenient to use and having reduced energy needs – for instance, by washing at lower temperatures.

Peroxygen sources such as hydrogen peroxide, with or without bleach activators, are used for removing stains, and improving the whiteness of light coloured fabrics during laundry. However, such agents tend to have lower efficacy at colder temperatures. A means to achieve better low temperature bleaching performance is through the use of organic bleach catalysts in combination with activated peroxygen sources. To maximize the bleaching efficiency, it is desirable to rapidly and uniformly distribute the bleach catalyst, and preferably the activated peroxygen source, into the wash. In addition, by rapidly and uniformly distributing the bleach catalyst and activated peroxygen source, fabric damage due to spot bleaching is avoided. A means to achieve this is to incorporate a bleaching system, comprising organic bleach catalysts and activated peroxygen sources, into a liquid laundry detergent composition. However, it remains challenging to prevent the activated peroxygen source from reacting with the organic bleach catalyst, or other sensitive laundry ingredients, in such aqueous laundry detergent compositions. These interactions can be minimized by keeping the ingredients dry, for instance, by incorporating them into powder detergents or tablets. However, dry laundry detergent forms are slower to disperse, and hence do not fully overcome the risk of spot bleaching. In addition, many consumers have a desire to avoid the additional step of filling a dosing device that is generally required, when using liquid laundry detergent compositions.

- 30 Accordingly, there remains a need for a convenient to use fluid laundry detergent, with a bleaching system, that is stable and suitable for use over a wide range of wash temperatures,

including low temperatures, while also virtually eliminating the risk of fabric damage due to spot bleaching.

SUMMARY OF THE INVENTION

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The present invention provides for a unit dose laundry detergent article comprising: an anionic and/or nonionic surfactant; and a bleaching system comprising: an organic bleach catalyst consisting of an aryliminium ion selected from the group: cations, zwitterions, and mixtures thereof; and an activated peroxygen source selected from the group consisting of: a preformed
10 peracid; a hydrogen peroxide source; and mixtures thereof; enclosed in a water-soluble or dispersible film, wherein: at least 50 % by weight of the anionic and/or nonionic surfactant, and at least 50 % by weight of the aryliminium ions are comprised in at least one fluid composition.

DETAILED DESCRIPTION OF THE INVENTION

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As used herein, "unit dose laundry detergent article" refers to any laundry treatment composition in single usage form. The unit dose laundry detergent article of the invention comprises at least one "fluid comprising compartment" and may optionally comprise a solid component. If present, the solid component may be in a separate compartment, suspended in a fluid-filled compartment,
20 or as part of a paste. A fluid-filled compartment refers to a partition of the unit dose laundry detergent article comprising a fluid capable of wetting a fabric e.g., clothing. The term, fluid, includes such forms as liquids, gels and pastes. The fluid contained in the fluid comprising compartment may include solids or gases in suitably subdivided form, but excludes forms which are non-fluid overall, such as tablets or granules.

25 All percentages, ratios and proportions used herein are by weight percent of the encapsulated portion of the unit dose laundry detergent article (including that of multiple compartments where appropriate), unless otherwise specified. That is, excluding the weight of the encapsulating material. All average values are calculated "by weight" of the encapsulated portion, unless otherwise expressly indicated. Unless otherwise specified, the pH is measured on the neat
30 composition, at 21°C, using a Thermo Electron Corporation Orion 261S pH meter with gel-filled probe (Orion Triode Combination pH/ATC probe, model # 9107WP), calibrated according to the instruction manual.

Unit dose laundry detergent articles:

Unit dose laundry detergent articles of the present invention comprise, in single, easy to use dosage form: an anionic and/or nonionic surfactant, an aryliminium ion, and an activated peroxygen source. Such unit dose articles have the benefit of ensuring that the correct dosages of the bleaching ingredients are delivered. For optimum bleaching performance, the amount of the aryliminium ion and the activated peroxygen source, as well as their ratio, is preferably carefully controlled. The unit dose laundry detergent article preferably also comprises anionic nonsoap surfactants; other surfactants, especially additional nonionic surfactants; non-aminofunctional organic solvents, and laundering adjuncts for improved cleaning and fabric care.

The unit dose laundry detergent article comprises one or more compartments. A multi-compartment unit dose form may be desirable for such reasons as: separating chemically incompatible ingredients; or where it is desirable for a portion of the ingredients to be released into the wash earlier or later.

Anionic and nonionic surfactants:

Detergent compositions of the present invention comprise, preferably from 1% to 70%, more preferably from 10% to 50%, and most preferably from 15% to 45% by weight of an anionic and/or nonionic surfactant.

Anionic surfactants: The unit dose laundry detergent articles of the present invention preferably comprise from 1 to 70 %, more preferably from 5 to 50 % by weight of one or more anionic surfactants. Preferred anionic surfactants are selected from the group consisting of: C11-C18 alkyl benzene sulfonates, C10-C20 branched-chain and random alkyl sulfates, C10-C18 alkyl ethoxy sulfates, mid-chain branched alkyl sulfates, mid-chain branched alkyl alkoxy sulfates, C10-C18 alkyl alkoxy carboxylates comprising 1-5 ethoxy units, modified alkylbenzene sulfonate, C12-C20 methyl ester sulfonate, C10-C18 alpha-olefin sulfonate, C6-C20 sulfosuccinates, and mixtures thereof. However, by nature, every anionic surfactant known in the art of detergent compositions may be used, such as disclosed in "Surfactant Science Series", Vol. 7, edited by W. M. Linfield, Marcel Dekker. However, the compositions of the present invention preferably comprise at least one sulphononic acid surfactant, such as a linear alkyl benzene sulphononic acid, or the water-soluble salt forms.

Anionic sulfonate or sulfonic acid surfactants suitable for use herein include the acid and salt forms of linear or branched C5-C20, more preferably C10-C16, most preferably C11-C13

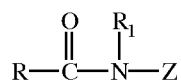
alkylbenzene sulfonates, C5-C20 alkyl ester sulfonates, C6-C22 primary or secondary alkane sulfonates, C5-C20 sulfonated polycarboxylic acids, and mixtures thereof. The aforementioned surfactants can vary widely in their 2-phenyl isomer content. Anionic sulphate salts suitable for use in compositions of the invention include: primary and secondary alkyl sulphates, having a
5 linear or branched alkyl or alkenyl moiety having from 9 to 22 carbon atoms, more preferably from 12 to 18 carbon atoms; beta-branched alkyl sulphate surfactants; and mixtures thereof. Mid-chain branched alkyl sulphates or sulfonates are also suitable anionic surfactants for use in the compositions of the invention. Preferred are the C5-C22, preferably C10-C20 mid-chain branched alkyl primary sulphates. When mixtures are used, a suitable average total number of
10 carbon atoms for the alkyl moieties is preferably within the range of from 14.5 to 17.5. Preferred mono-methyl-branched primary alkyl sulphates are selected from the group consisting of the 3-methyl to 13-methyl pentadecanol sulphates, the corresponding hexadecanol sulphates, and mixtures thereof. Dimethyl derivatives or other biodegradable alkyl sulphates having light branching can similarly be used. Other suitable anionic surfactants for use herein include fatty
15 methyl ester sulphonates and/or alkyl ethoxy sulphates (AES) and/or alkyl polyalkoxylated carboxylates (AEC). Mixtures of anionic surfactants can be used, for example mixtures of alkylbenzenesulphonates and AES.

The anionic surfactants are typically present in the form of their salts with alkanolamines or alkali metals such as sodium and potassium. Preferably, the anionic surfactants are neutralized with
20 alkanolamines, such as monoethanolamine or triethanolamine, and are fully soluble in the fluid phase.

Nonionic surfactants: The unit dose laundry detergent articles of the present invention may include from 1 to 70 %, preferably from 5 to 50 % by weight of a nonionic surfactant. Suitable nonionic surfactants include, but are not limited to C12-C18 alkyl ethoxylates ("AE") including
25 the so-called narrow peaked alkyl ethoxylates, C6-C12 alkyl phenol alkoxyates (especially ethoxylates and mixed ethoxy/propoxy), block alkylene oxide condensate of C6-C12 alkyl phenols, alkylene oxide condensates of C8-C22 alkanols and ethylene oxide/propylene oxide block polymers (Pluronic®-BASF Corp.), as well as semi polar nonionics (e.g., amine oxides and phosphine oxides). An extensive disclosure of suitable nonionic surfactants can be found in U.S.
30 Pat. 3,929,678.

Alkylpolysaccharides such as disclosed in U.S. Pat. 4,565,647 are also useful nonionic surfactants for compositions of the invention. Also suitable are alkyl polyglucoside surfactants. In some

embodiments, suitable nonionic surfactants include those of the formula $R_1(OC_2H_4)_nOH$, wherein R_1 is a C10-C16 alkyl group or a C8-C12 alkyl phenyl group, and n is from 3 to 80. In some embodiments, the nonionic surfactants may be condensation products of C12-C15 alcohols with from 5 to 20 moles of ethylene oxide per mole of alcohol, e.g., C12-C13 alcohol condensed with about 6.5 moles of ethylene oxide per mole of alcohol. Additional suitable nonionic surfactants include polyhydroxy fatty acid amides of the formula:



wherein R is a C9-C17 alkyl or alkenyl, R_1 is a methyl group and Z is glycidyl derived from a reduced sugar or alkoxyated derivative thereof. Examples are N-methyl N-1-deoxyglucityl cocoamide and N-methyl N-1-deoxyglucityl oleamide.

Bleaching systems:

The unit dose laundry detergent article comprises an organic bleach catalyst and an activated peroxygen source. Such organic bleach catalysts improve the bleaching performance, particularly at low temperatures. They are capable of accepting an oxygen atom from an activated peroxygen source and transferring the oxygen atom to an oxidizable substrate.

The organic bleach catalyst of the present invention comprises an aryliminium ion. The aryliminium ions may be cations, zwitterions, or a mixture thereof. To ensure rapid distribution of the aryliminium ions throughout the wash, at least 50%, preferably at least 80%, more preferably 100%, by weight of the aryliminium ions are comprised in the fluid comprising compartment of the unit dose laundry detergent article. The unit dose laundry detergent article may comprise from 0.001% to 10%, preferably from 0.01% to 5%, more preferably from 0.1% to 2% by weight percent of the aryliminium ion. The unit dose laundry detergent article may comprise from 0.1% to 30%, preferably from 0.5% to 20%, more preferably from 1% to 10% by weight percent of the activated peroxygen source. The aryliminium ions of the present invention react with activated peroxygen sources such as peracids to form aryloxaziridinium ions, which bleach oxidizable substrates.

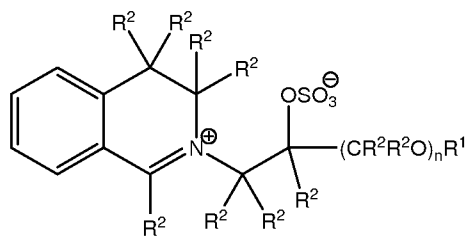
In order to maximize the benefit of the aryliminium ion, and minimize its decomposition, the unit dose laundry detergent article preferably comprises a weight ratio of the aryliminium ion to activated peroxygen source of from 2:1 to 1:500, preferably from 1:1 to 1:100, more preferably from 1:5 to 1:50, still more preferably from 1:10 to 1:30.

In addition, the stability of the aryliminium ions (and resultant aryloxaziridinium ions) is affected by the wash temperature at dilutions typically found in the wash liquor. At lower wash temperatures, such as from 5 °C to 30 °C, the decomposition rate of the organic bleach catalyst is reduced, compared to at higher wash temperatures, such as above 40 °C. In contrast, typical
 5 bleaching agents, such as peroxides with or without bleach activators, are less effective at reduced wash temperatures. Therefore, aryliminium ions are particularly useful for improving the efficacy of bleaching systems for low temperature laundry applications.

The bleaching system for use in the present invention may also include other bleaching agents
 10 such as: bleach activators, metal-containing bleach catalysts, transition metal complexes of macropolycyclic rigid ligands, and mixtures thereof.

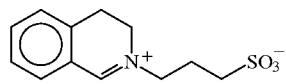
1) Organic bleach catalyst:

Aryliminium zwitterions: Suitable aryliminium zwitterions maybe selected from the group consisting of:



(Figure 1)

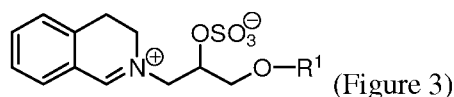
wherein: in figure 1, R¹ is selected from the group consisting of: H, a branched alkyl group containing from 3 to 24 carbons, and a linear alkyl group containing from 1 to 24 carbons. Preferably, R¹ is a branched alkyl group comprising from 6 to 18 carbons, or a linear alkyl group comprising from 5 to 18 carbons, more preferably each R¹ is selected from the group consisting
 20 of: 2-propylheptyl, 2-butyloctyl, 2-pentylononyl, 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; n is an integer from 0 to 1;



(Figure 2)

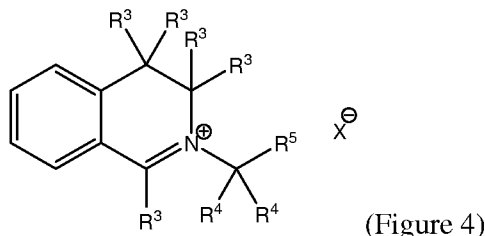
3-(3,4-dihydroisoquinolinium)propane sulfonate;
 and mixtures thereof.

More preferably, the aryliminium zwitterions have the structure:



wherein: in Figure 3, R¹ is a branched alkyl group containing from 9 to 24 carbons or linear alkyl group containing from 11 to 24 carbons, preferably, each R¹ is a branched alkyl group containing from 9 to 18 carbons or linear alkyl group containing from 11 to 18 carbons, more preferably each R¹ is selected from the group consisting of 2-propylheptyl, 2-butyloctyl, 2-pentynonyl, 2-hexyldecyl, n-dodecyl, n-tetradecyl, n-hexadecyl, n-octadecyl, iso-nonyl, iso-decyl, iso-tridecyl and iso-pentadecyl. Suitable aryliminium zwitterions include those listed in Table 1a, Table 1b, and mixtures thereof. Preferred aryliminium zwitterions are those listed in Table 1b, and mixtures thereof. Most preferred, are the inner salts of 3-(3,4-dihydroisoquinolinium) propane sulfonate, sulphuric acid mono-[2-(3,4-dihydro-isoquinolin-2-yl)-1-(2-butyl-octyloxymethyl)-ethyl] ester, and mixtures thereof. Other suitable examples of organic bleach catalysts can be found in US 5,576,282 and US 5,817,614, EP 923,636 B1, WO 2001/16263 A1, WO 2000/42156 A1, WO 2007/001262 A1.

Aryliminium cations: Suitable cations and polycations include aryliminium ions having the structure:



wherein: in figure 4, R³ is independently selected from the group consisting of: H and methyl groups. Preferably, R³ is H. R⁴ and R⁵ are independently selected from the group consisting of: H, a branched alkyl group containing from 3 to 12 carbons, and a linear alkyl group containing from 1 to 12 carbons. Preferably, R⁴ and R⁵ are H or methyl, more preferably, R⁴ and R⁵ are H. X⁻ is a charge-balancing counterion; preferably a bleach-compatible counterion. Suitable aryliminium cations include those listed in Table 2, and mixtures thereof. Most preferred, are *N*-methyl-3,4-dihydroisoquinolinium tetrafluoroborate, *N*-methyl-3,4-dihydroisoquinolinium *p*-toluene sulphonate, and mixtures thereof.

The stability of the aryliminium ion is improved when the fluid comprising compartment that contains the aryliminium ion has a neat pH of less than 9, preferably less than 8.5, more

preferably less than 8, even more preferably less than 7. In another preferred embodiment, the pH of the fluid comprising compartment that contains the aryliminium ion is from 5 to 7.

2) Activated peroxygen sources:

Activated peroxygen sources supply the oxygen atoms that are transferred to the oxidizable substrate and as such, are an essential feature of the bleaching system. The activated peroxygen source is selected from the group consisting of: a preformed peracid, a hydrogen peroxide source, and mixtures thereof.

For improved stability before use, the activated peroxygen source is preferably at least partially physically separated from the aryliminium ions, such that the activated peroxygen source and organic bleach catalyst are unable to interact chemically. In one embodiment, at least 50%, preferably 80%, more preferably 100%, by weight of the activated peroxygen source is a solid. In such embodiments, catalyzed degradation of the peroxygen source by the aryliminium ions is inhibited by the solid-liquid phase boundary. In another embodiment, at least 50%, preferably 80%, more preferably 100%, by weight of the activated peroxygen source is encapsulated by a water-soluble or dispersible barrier which keeps the majority of the activated peroxygen source isolated from the aryliminium ions. Suitable water-soluble or dispersible barrier materials include carbohydrates, natural or synthetic gums, chitin and chitosan, cellulose and cellulose derivatives, polyvinyl alcohol and polyvinyl alcohol derivatives, polyvinyl acetate, polyethylene glycol, synthetic and natural waxes, gelatin, alginates, acrylic polymers and their derivatives, starch materials, an inorganic coating (silicates, phosphates, carbonates, zeolites, alumina and mixtures thereof), urea-formaldehyde, melamine-formaldehyde, fatty acids, polyurethanes, polyamides, polyureas, polyesters and mixtures thereof. In yet another embodiment, at least 50%, preferably at least 80%, more preferably 100%, by weight of the activated peroxygen source is in a different compartment comprising less than 25%, preferable less than 10%, more preferably, less than 1%, by weight of the aryliminium ions.

By a similar means, the activated peroxygen source can be physically separated from ingredients such as enzymes and perfumes that are sensitive to bleaching agents. Such embodiments include unit dose laundry detergent articles, further comprising a deterative enzyme selected from the group consisting of: lipase, protease, amylase, cellulase, pectate lyase, xyloglucanase, and mixtures thereof; wherein at least part of the activated peroxygen source is physically separated from the deterative enzyme by a means selected from the group consisting of: at least 50%, preferably 80%, more preferably 100%, by weight of the activated peroxygen source being a

solid; at least 50%, preferably 80%, more preferably 100%, by weight of the activated peroxygen source being encapsulated by a water-soluble or dispersible barrier; and at least 50%, preferably 80%, more preferably 100%, by weight of the activated peroxygen source being in a different compartment comprising less than 25%, preferable less than 10%, more preferably, less than 1%,
5 by weight of the deterative enzymes. In another such embodiment, the unit dose laundry detergent articles, further comprising a perfume; wherein at least part of the activated peroxygen source is physically separated from the perfume by a means selected from the group consisting of: at least 50%, preferably 80%, more preferably 100%, by weight of the activated peroxygen source being a solid; at least 50%, preferably 80%, more preferably 100%, by weight of the activated
10 peroxygen source being encapsulated by a water-soluble or dispersible barrier; and at least 50%, preferably 80%, more preferably 100%, by weight of the activated peroxygen source being in a different compartment comprising less than 25%, preferable less than 10%, more preferably, less than 1%, by weight of the perfume.

Preformed peracids: Suitable preformed peracids include, but are not limited to, compounds
15 selected from the group consisting of: phthalimido peroxyacaproic acid (PAP), percarboxylic acids and salts, percarbonic acids and salts, perimidic acids and salts, peroxymonosulphuric acids and salts, and mixtures thereof. Phthalimido peroxyacaproic acid (PAP) is preferred. A suitable salt of a peroxymonosulphuric acid is potassium peroxymonosulphate (potassium monopersulphate), or its triple salt: $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$.

20 The stability of fluid comprising compartments containing a preformed peracid, is improved by having a neat pH of from 4 to 10, preferably from 6.5 to 9, more preferably from 7 to 8.5. For instance, peracids such as phthalimido peroxyacaproic acid are less prone to ring-opening in such a pH range. It is believed that more of the peracid is protonated in this pH range, resulting in slower availability of the peracid. This gives more time for the organic bleach booster to distribute over
25 the substrate, leading to improved stain bleaching.

In unit dose laundry detergent articles, the preformed peracid may be present at a level of from 0.1% to 30%, preferably from 0.5% to 25%, more preferably from 1% to 10%, most preferably from 2% to 4% by weight of the encapsulated portion of the unit dose laundry detergent article. Alternatively, for unit dose laundry detergent articles for use primarily as a bleach additive, an
30 even higher level of peracid may be present. For instance, such compositions may comprise from 10% to 40%, preferably from 15% to 30%, more preferably from 15% to 25%, by weight preformed peracid. In one multi-compartment embodiment having improved stability, at least

80% by weight of the preformed peracid is encapsulated in a compartment comprising less than 25% by weight of the aryliminium ions.

Hydrogen peroxide sources: Suitable hydrogen peroxide sources include: peroxides, persalts, and mixtures thereof. Embodiments of the invention may comprise from 0.1% to 30%, preferably
5 from 0.5% to 20%, more preferably from 1% to 10% by weight of a hydrogen peroxide source.

Hydrogen peroxide is one of the most powerful oxidizers known. It is a very selective bleaching agent causing less textile fibre damage compared to many other peroxygen sources and tends to be less aggressive on fabric dyes, detergent enzymes and optical brighteners. When incorporated into unit dose laundry detergent articles of the invention, add-on levels of 0.1% to 10%,
10 preferably 0.5 to 5%, by weight of hydrogen peroxide are preferred. Suitable peroxides also include organic peroxides, such as diacyl peroxides, that do not cause visible spotting or filming. One example is dibenzoyl peroxide. Other suitable hydrogen peroxide sources are described in detail in Kirk Othmer's Encyclopaedia of Chemical Technology, 4th Ed (1992, John Wiley & Sons), Vol. 4, pp. 271-300 "Bleaching Agents (Survey)".

15 Suitable persalts include: percarbonates, perborates, persulphates, perphosphates, persilicates. Percarbonates and perborates are preferred. Percarbonates are particularly preferred for their greater rate of dissolution, a more environmentally friendly profile and the advantage of concurrently generating hydrogen peroxide, while also liberating carbonate. Thus, they give a higher pH than perborates and favour perhydrolysis. Sodium percarbonate is a suitable
20 percarbonate. Perborate sources, such as sodium perborate, have good stability and selectivity. Other preferred perborate sources include the tetrahydrate and/or the monohydrate. For improved stability, the persalt may be coated.

3) Other bleaching agents:

Bleach Activators: The bleaching system of the present invention can be formulated with a bleach
25 activator in combination with a persalt and/or peroxide. Persalts, particularly percarbonates and/or perborates, are preferred. An example of a suitable peroxide is dibenzoyl peroxide. When used, the bleach activator is preferably selected from the group consisting of: nonanoyloxybenzene sulphonate (NOBS), sodium 4-(isononanyloxy)benzenesulphonate (iso-NOBS), tetraacetyl ethylene diamine (TAED) or mixtures thereof. They may be present at levels of from 0.01 to 15
30 %, preferably from 0.5 to 10 %, more preferably from 1% to 8 % by weight. When lipase enzymes are incorporated into the unit dose laundry detergent article, sodium 4-(isononanyloxy)benzenesulphonate is particularly preferred, since, unlike other bleach

activators, it is highly compatible with lipase. The diacyl peroxide (DAP) formed from the reaction of iso-NOBS with the C9 peroxyacid generated from iso-NOBS is also compatible with lipase. Other suitable bleach activators may be selected from the group consisting of: benzoylcaprolactam (BzCL), 4-nitrobenzoylcaprolactam, 3-chlorobenzoyl-caprolactam, benzoyloxybenzenesulphonate (BOBS), phenyl benzoate (PhBz), decanoyloxybenzenesulphonate (C10-OBS), benzoylvalerolactam (BZVL), octanoyloxybenzenesulphonate (C8-OBS), perhydrolyzable esters and mixtures thereof, alternatively benzoylcaprolactam and benzoylvalerolactam, 4-[N-(nonaoyl) amino hexanoyloxy]-benzene sulfonate sodium salt (NACA-OBS) (See U.S. 5,523,434), dodecanoyloxy-benzenesulphonate (LOBS or C12-OBS), 10-undecenoyloxybenzenesulfonate (UDOBS or C11-OBS with unsaturation in the 10 position), and decanoyloxybenzoic acid (DOBA) and mixtures thereof. Non-limiting examples of suitable bleach activators, including quaternary substituted bleach activators, are described in US 6,855,680. Alternatively, the aryliminium ion may be selected to incorporate bleach activation properties.

Metal-containing Bleach Catalysts: Preferred bleach catalysts include manganese and cobalt-containing bleach catalysts. Other suitable metal-containing bleach catalysts include catalyst systems comprising a transition metal cation of defined bleach catalytic activity, such as copper, iron, titanium, ruthenium tungsten, molybdenum, or manganese cations; an auxiliary metal cation having little or no bleach catalytic activity, such as zinc or aluminium cations; and a sequesterant having defined stability constants for the catalytic and auxiliary metal cations, particularly ethylenediaminetetraacetic acid, ethylenediaminetetra (methylenephosphonic acid) and water-soluble salts thereof. Suitable catalyst systems are disclosed in US 4,430,243.

Transition Metal Complexes: The unit dose laundry detergent articles herein may also include bleach catalysts comprising a transition metal complex, preferably of a macropolycyclic rigid ligand. The amount used is preferably from 0.0001% to 5%, more preferably from 0.001% to 2%, most preferably from 0.01% to 1% by weight of the encapsulated portion of the unit dose laundry detergent article.

Laundering adjuncts:

The unit dose laundry detergent article of the present invention may also include conventional laundry detergent ingredients selected from the group consisting of: additional surfactants, non-aminofunctional organic solvents, enzymes, enzyme stabilizers, amphiphilic alkoxyated grease cleaning polymers, clay soil cleaning polymers, soil release polymers, soil suspending polymers,

bleaching systems, optical brighteners, hueing dyes, particulate material, perfume and other odour control agents, hydrotropes, suds suppressors, fabric care benefit agents, pH adjusting agents, dye transfer inhibiting agents, preservatives, non-fabric substantive dyes and mixtures thereof. Some of the optional ingredients which can be used are described in greater detail as follows:

5 *Additional Surfactants:* The unit dose laundry detergent articles of the present invention may comprise additional surfactant selected from the group consisting: anionic, cationic, nonionic, amphoteric and/or zwitterionic surfactants and mixtures thereof.

Suitable cationic surfactants can be water-soluble, water-dispersible or water-insoluble. Such cationic surfactants have at least one quaternized nitrogen and at least one long-chain hydrocarbyl
10 group. Compounds comprising two, three or even four long-chain hydrocarbyl groups are also included. Examples include alkyltrimethylammonium salts, such as C12 alkyltrimethylammonium chloride, or their hydroxyalkyl substituted analogues. The present invention may comprise 1% or more of cationic surfactants.

Amphoteric deterative surfactants suitable for use in the composition include those surfactants
15 broadly described as derivatives of aliphatic secondary and tertiary amines in which the aliphatic radical can be straight or branched chain and wherein one of the aliphatic substituents contains from 8 to 18 carbon atoms and one contains an anionic group such as carboxy, sulphonate, sulphate, phosphate, or phosphonate. Suitable amphoteric deterative surfactants for use in the present invention include, but are not limited to: cocoamphoacetate, cocoamphodiacetate,
20 lauroamphoacetate, lauroamphodiacetate, and mixtures thereof.

Zwitterionic deterative surfactants suitable for use in unit dose laundry detergent articles are well known in the art, and include those surfactants broadly described as derivatives of aliphatic quaternary ammonium, phosphonium, and sulphonium compounds, in which the aliphatic radicals can be straight or branched chain, and wherein one of the aliphatic substituents contains
25 from 8 to 18 carbon atoms and one contains an anionic group such as carboxy, sulfonate, sulphate, phosphate or phosphonate. Zwitterionics such as betaines are also suitable for this invention. Furthermore, amine oxide surfactants having the formula:
 $R(EO)_x(PO)_y(BO)_zN(O)(CH_2R')_2 \cdot qH_2O$ are also useful in compositions of the present invention. R is a relatively long-chain hydrocarbyl moiety which can be saturated or unsaturated, linear or
30 branched, and can contain from 8 to 20, preferably from 10 to 16 carbon atoms, and is more preferably C12-C16 primary alkyl. R' is a short-chain moiety preferably selected from hydrogen, methyl and -CH₂OH. When x+y+z is different from 0, EO is ethyleneoxy, PO is propyleneoxy

and BO is butyleneoxy. Amine oxide surfactants are illustrated by C12-C14 alkyldimethyl amine oxide.

Non-limiting examples of other anionic, zwitterionic, amphoteric or optional additional surfactants suitable for use in the compositions are described in McCutcheon's, Emulsifiers and
5 Detergents, 1989 Annual, published by M. C. Publishing Co., and U.S. Pat. Nos. 3,929,678, 2,658,072; 2,438,091; 2,528,378.

Water and/or Non-aminofunctional organic solvent: The fluid comprising compartments of the unit dose laundry detergent article preferably comprise less than 20%, more preferably less than 15%, most preferably less than 10% by weight water. Alternatively, the fluid comprising
10 compartment may be almost entirely non-aqueous, preferably comprising from 2% to 40 %, more preferably from 5 to 25 % by weight of a non-aminofunctional organic solvent. Such fluid comprising compartments may comprise very little water, for instance, that which is introduced with other raw materials.

As used herein, "non-aminofunctional organic solvent" refers to any organic solvent which
15 contains no amino functional groups. Preferred non-aminofunctional organic solvents include monohydric alcohols, dihydric alcohols, polyhydric alcohols, glycerol, glycols, polyalkylene glycols such as polyethylene glycol, and mixtures thereof. Highly preferred are mixtures of solvents, especially mixtures of two or more of the following: lower aliphatic alcohols such as ethanol, propanol, butanol, isopropanol; diols such as 1,2-propanediol or 1,3-propanediol; and
20 glycerol. Also preferred are propanediol and mixtures thereof with diethylene glycol where the mixture contains no methanol or ethanol. Thus embodiments of unit dose laundry detergent articles of the present invention may include embodiments in which propanediols are used but methanol and ethanol are not used.

Preferable non-aminofunctional organic solvents are liquid at ambient temperature and pressure
25 (i.e. 21°C and 1 atmosphere), and comprise carbon, hydrogen and oxygen. Non-aminofunctional organic solvents may be present when preparing a premix of the external structuring system, or in the final unit dose laundry detergent article.

Enzymes: The unit dose laundry detergent articles of the present invention may comprise from 0.0001 % to 8 % by weight of a deterative enzyme which provides cleaning performance and/or
30 fabric care benefits. Such compositions preferably have a composition pH of from 6 to 10.5. Suitable enzymes can be selected from the group consisting of: lipase, protease, amylase, cellulase, pectate lyase, xyloglucanase, and mixtures thereof. A preferred enzyme combination

comprises a cocktail of conventional detergent enzymes such as lipase, protease, cellulase and amylase. Detergent enzymes are described in greater detail in U.S. Patent No. 6,579,839.

Enzyme Stabilizers: Enzymes can be stabilized using any known stabilizer system such as calcium and/or magnesium compounds, boron compounds and substituted boric acids, aromatic borate esters, peptides and peptide derivatives, polyols, low molecular weight carboxylates, relatively hydrophobic organic compounds [e.g. certain esters, dialkyl glycol ethers, alcohols or alcohol alkoxylates], alkyl ether carboxylate in addition to a calcium ion source, benzamidine hypochlorite, lower aliphatic alcohols and carboxylic acids, N,N-bis(carboxymethyl) serine salts; (meth)acrylic acid-(meth)acrylic acid ester copolymer and PEG; lignin compound, polyamide oligomer, glycolic acid or its salts; poly hexamethylene biguanide or N,N-bis-3-amino-propyl-dodecyl amine or salt; and mixtures thereof.

Polymer Deposition Aids: Preferably, the unit dose laundry detergent article comprises from 0.1% to 7%, more preferably from 0.2% to 3%, of a polymer deposition aid. As used herein, "polymer deposition aid" refers to any cationic polymer or combination of cationic polymers that significantly enhance deposition of a fabric care benefit agent onto the fabric during laundering. Suitable polymer deposition aids can comprise a cationic polysaccharide and/or a copolymer. "Fabric care benefit agent" as used herein refers to any material that can provide fabric care benefits. Non-limiting examples of fabric care benefits include, but are not limited to: fabric softening, colour protection, colour restoration, pill/fuzz reduction, anti-abrasion and anti-wrinkling. Non-limiting examples of fabric care benefit agents include: silicone derivatives, oily sugar derivatives, dispersible polyolefins, polymer latexes, cationic surfactants and combinations thereof.

Cleaning Polymers: The unit dose laundry detergent articles herein may optionally contain from 0.01 to 20% by weight of one or more cleaning polymers that provide for broad-range soil cleaning of surfaces and fabrics and/or suspension of the soils. Any suitable cleaning polymer may be of use. Useful cleaning polymers are described in US 2009/0124528A1. Non-limiting examples of useful categories of cleaning polymers include: amphiphilic alkoxylated grease cleaning polymers; clay soil cleaning polymers; soil release polymers; and soil suspending polymers.

Optical brighteners: These are also known as fluorescent whitening agents for textiles. Preferred levels are from 0.001% to 2% by weight of the encapsulated portion of the unit dose laundry detergent article. Suitable brighteners are disclosed in EP 686691B and include

hydrophobic as well as hydrophilic types. Brightener 49 is preferred for use in the present invention.

Hueing dyes: Hueing dyes or fabric shading dyes are useful laundering adjuncts in unit dose laundry detergent articles. Suitable dyes include blue and/or violet dyes having a hueing or shading effects. See, for example, WO 2009/087524 A1, WO2009/087034A1 and references therein. Recent developments that are suitable for the present invention include sulfonated phthalocyanine dyes having a zinc or aluminium central atom. The unit dose laundry detergent articles herein may comprise from 0.00003% to 0.1%, preferably from 0.00008% to 0.05% by weight of the fabric hueing dye.

Particulate material: The unit dose laundry detergent article may include particulate material such as clays, suds suppressors, encapsulated oxidation-sensitive and/or thermally sensitive ingredients such as perfumes (perfume microcapsules), bleaches and enzymes; or aesthetic adjuncts such as pearlescent agents including mica, pigment particles, or the like. Suitable levels are from 0.0001% to 10%, or from 0.1% to 5% by weight of the encapsulated portion of the unit dose laundry detergent article.

Perfume and other odour control agents: In preferred embodiments, the unit dose laundry detergent article comprises a free and/or micro-encapsulated perfume. If present, the free perfume is typically incorporated at a level from 0.001 to 10%, preferably from 0.01% to 5%, more preferably from 0.1% to 3% by weight of the encapsulated portion of the unit dose laundry detergent article.

By encapsulating at least part of the perfume raw materials in a perfume microcapsule, the perfume raw materials can be protected from oxidation by the bleach system. If present, the perfume microcapsule is formed by at least partially surrounding the perfume raw materials with a wall material. Preferably, the microcapsule wall material comprises: melamine crosslinked with formaldehyde, polyurea, urea crosslinked with formaldehyde or urea crosslinked with gluteraldehyde. Suitable perfume microcapsules and perfume nanocapsules include those described in the following references: US 2003215417 A1; US 2003216488 A1; US 2003158344 A1; US 2003165692 A1; US 2004071742 A1; US 2004071746 A1; US 2004072719 A1; US 2004072720 A1; EP 1393706 A1; US 2003203829 A1; US 2003195133 A1; US 2004087477 A1; US 20040106536 A1; US 6645479; US 6200949; US 4882220; US 4917920; US 4514461; US RE 32713; US 4234627.

In other embodiments, the unit dose laundry detergent article comprises odour control agents such as uncomplexed cyclodextrin, as described in US 5,942,217. Other suitable odour control agents include those described in: US 5,968,404, US 5,955,093, US 6,106,738, US 5,942,217, and US 6,033,679.

- 5 *Hydrotropes:* The encapsulated portion of the unit dose laundry detergent article typically comprises a hydrotrope in an effective amount, preferably up to 15%, more preferably from 1 % to 10 %, most preferably from 3 % to 6 % by weight, so that the fluid laundry detergent compositions are compatible in water. Suitable hydrotropes for use herein include anionic-type hydrotropes, particularly sodium, potassium, and ammonium xylene sulfonate, sodium, potassium
10 and ammonium toluene sulfonate, sodium potassium and ammonium cumene sulfonate, and mixtures thereof, as disclosed in US 3,915,903.

External structuring system: An external structuring system is a compound or mixture of compounds which provide either a sufficient yield stress or low shear viscosity to stabilize the fluid independently from, or extrinsic from, the structuring effect of any deterative surfactants in
15 the composition. The fluid within any compartment of the present invention may comprise from 0.01% to 5%, preferably from 0.1% to 1% by weight of an external structuring system. Suitable external structuring systems include non-polymeric crystalline, hydroxy-functional structurants, polymeric structurants, or mixtures thereof.

Preferably, the external structurant system imparts a high shear viscosity at 20 s^{-1} at 21°C of from
20 1 to 1500 cps, and a viscosity at low shear (0.05 s^{-1} at 21°C) of greater than 5000 cps. The viscosity is measured using an AR 550 rheometer from TA instruments using a plate steel spindle at 40 mm diameter and a gap size of 500 μm . The high shear viscosity at 20 s^{-1} and low shear viscosity at 0.5 s^{-1} can be obtained from a logarithmic shear rate sweep from 0.1 s^{-1} to 25 s^{-1} in 3 minutes time at 21°C .

- 25 The external structuring system may comprise from 0.01 to 1% by weight of a non-polymeric crystalline, hydroxyl functional structurant. Such non-polymeric crystalline, hydroxyl functional structurants generally comprise a crystallisable glyceride which can be pre-emulsified to aid dispersion into the final unit dose laundry detergent article. Preferred crystallisable glycerides include hydrogenated castor oil or "HCO" or derivatives thereof, provided that it is capable of
30 crystallizing in the fluid detergent composition. Other embodiments of suitable external structuring systems may comprise from 0.01 to 5% by weight of a naturally derived and/or synthetic polymeric structurant. Examples of suitable naturally derived polymeric structurants

include: hydroxyethyl cellulose, hydrophobically modified hydroxyethyl cellulose, carboxymethyl cellulose, polysaccharide derivatives and mixtures thereof. Suitable polysaccharide derivatives include: pectine, alginate, arabinogalactan (gum Arabic), carrageenan, gellan gum, xanthan gum, guar gum and mixtures thereof. Examples of suitable synthetic polymeric structurants include:

5 polycarboxylates, polyacrylates, hydrophobically modified ethoxylated urethanes, hydrophobically modified non-ionic polyols and mixtures thereof.

Unit dose pouch material:

The contents of the unit-dose compartments can generally be prepared by mixing the ingredients together. The contents of the unit-dose compartments are enclosed in a water-soluble or dispersible film. The water-soluble or dispersible film preferably has a water-solubility of at least

10 50%, more preferably at least 75% or even at least 95%. The water-solubility is measured by the method set out here: 5.0 grams $\pm$ 0.1 gram of the water-soluble or dispersible film is added in a pre-weighed 400 ml beaker and 245ml $\pm$ 1ml of distilled water is added. This is stirred vigorously on a magnetic stirrer set at 600 rpm, for 30 minutes. Then, the mixture is filtered

15 through a sintered-glass filter with a pore size of maximum 20 microns. The water is dried off from the collected filtrate by any conventional method, and the weight of the remaining material is determined (which is the dissolved or dispersed fraction). Then, the percentage solubility or dispersibility can be calculated.

Preferred polymers, copolymers or derivatives thereof suitable for use as water-soluble or dispersible films are selected from: polyvinyl pyrrolidone, polyalkylene oxides, acrylamide,

20 acrylic acid, cellulose, cellulose ethers, cellulose esters, cellulose amides, polyvinyl acetates, polycarboxylic acids and salts, polyaminoacids or peptides, polyamides, polyacrylamide, copolymers of maleic/acrylic acids, polysaccharides including starch and gelatine, natural gums such as xanthan and carragum. More preferred polymers are selected from polyacrylates and

25 water-soluble acrylate copolymers, methylcellulose, carboxymethylcellulose sodium, dextrin, ethylcellulose, hydroxyethyl cellulose, hydroxypropyl methylcellulose, maltodextrin, polymethacrylates, and most preferred are: polyvinyl alcohols, polyvinyl alcohol copolymers, hydroxypropyl methyl cellulose (HPMC), and combinations thereof. However, the high solubility of films comprising polyvinyl alcohol, polyvinyl alcohol copolymers, or mixtures thereof, makes

30 them especially preferred for use in the present invention. Such films dissolve particularly swiftly, such that the aryliminium ions are able to distribute rapidly and uniformly throughout the wash. Preferably, the level of polymer in the pouch material, for example a PVA polymer, is at least

60%. The polymer can have any weight average molecular weight, preferably from 1000 to 1,000,000, more preferably from 10,000 to 300,000 yet more preferably from 20,000 to 150,000.

EXAMPLES

5 Table 1a: Examples of aryliminium zwitterions suitable for use in the present invention:

3,4-dihydro-2-[2-(sulfooxy)decyl]isoquinolinium
3,4-dihydro-2-(2-sulfodecyl)- isoquinolinium, inner salt
3,4-dihydro-4,4-dimethyl-2-(2-sulfooctyl)- isoquinolinium, inner salt

Table 1b: Preferred aryliminium zwitterions for use in the present invention:

3-(3,4-dihydroisoquinolinium) propane sulfonate, internal salt
Sulphuric acid mono-[2-(3,4-dihydro-isoquinolin-2-yl)-1-(2-propylheptyloxymethyl)-ethyl] ester, internal salt
Sulphuric acid mono-[2-(3,4-dihydro-isoquinolin-2-yl)-1-(2-butyl-octyloxymethyl)-ethyl] ester, internal salt
Sulphuric acid mono-[2-(3,4-dihydro-isoquinolin-2-yl)-1-(2-pentyl-nonyloxymethyl)-ethyl] ester, internal salt
Sulphuric acid mono-[2-(3,4-dihydro-isoquinolin-2-yl)-1-(2-hexyl-decyloxymethyl)-ethyl] ester, internal salt
Sulphuric acid mono-[2-(3,4-dihydro-isoquinolin-2-yl)-1-(dodecyloxymethyl)-ethyl] ester, internal salt
Sulphuric acid mono-[2-(3,4-dihydro-isoquinolin-2-yl)-1-(tetradecyloxymethyl)-ethyl] ester, internal salt
Sulphuric acid mono-[2-(3,4-dihydro-isoquinolin-2-yl)-1-(hexadecyloxymethyl)-ethyl] ester, internal salt
Sulphuric acid mono-[2-(3,4-dihydro-isoquinolin-2-yl)-1-(octadecyloxymethyl)-ethyl] ester, internal salt
Sulphuric acid mono-[2-(3,4-dihydro-isoquinolin-2-yl)-1-(iso-nonyloxymethyl)-ethyl] ester, internal salt
Sulphuric acid mono-[2-(3,4-dihydro-isoquinolin-2-yl)-1-(iso-decyloxymethyl)-ethyl] ester, internal salt
Sulphuric acid mono-[2-(3,4-dihydro-isoquinolin-2-yl)-1-(iso-tridecyloxymethyl)-ethyl] ester, internal salt

Table 2: Examples of aryliminium cations suitable for use in the present invention:

N-methyl-3,4-dihydroisoquinolinium tetrafluoroborate
N- methyl-3,4-dihydroisoquinolinium p-toluene sulphonate
N-octyl-3,4-dihydroisoquinolinium p-toluene sulphonate
3,4-dihydro-2,3,3-trimethyl-isoquinolinium tetrafluoroborate
3,4-dihydro-2,4,4-trimethyl-isoquinolinium tetrafluoroborate
2-(1,1-dimethylethyl)-3,4-dihydro-isoquinolinium tetraphenylborate

Example 1a and 1b: Single compartment unit-dose laundry detergent articles of the present invention, encapsulated in a polyvinyl alcohol film.

	Example 1a	Example 1b
Ingredient name	Compartment 1	Compartment 1
	38 g	38 g
	WT %	WT %
Linear alkyl benzene sulfonic acid	14.8	14.8
Phthalimido peroxyacaproic acid (PAP) ¹	20	20
C12-14 alkyl ethoxy 3 sulphate MEA salt	8.8	8.8
Sulphuric acid mono-[2-(3,4-dihydro-isoquinolin-2-yl)-1-(2-butyl-octyloxymethyl)-ethyl] ester, internal salt	0.04	--
N-methyl-3,4-dihydroisoquinolinium p-toluene sulphonate	--	0.04
C12-14 alkyl 7-ethoxylate	13.0	13.0
C12-18 Fatty acid	10.0	10.0
Enzymes ²	2.3	2.3
PEG-PVAc polymer	2.0	2.0
Monoethanol amine	To pH 7.5	To pH 7.5
Mineral Oil	--	--
Water	9.5	9.5
Solvent	18	18
Miscellaneous/Minors	To 100	To 100

¹ Encapsulated according to the method in WO2006/120405 A1

5 ² Amylase and protease

Example 2a and 2b: Single compartment unit-dose laundry detergent articles of the present invention, encapsulated in a polyvinyl alcohol film.

	Example 2a	Example 2b
Ingredient name	Compartment 1	Compartment 1
	40 g	40 g
	WT %	WT %
LAS Na salt	21.7	21.7
C12-16EO5 alcohol ethoxylate	18.98	18.98
Butoxy-propoxy-propanol	18.98	18.98
Sodium Citrate	1.42	1.42
Sulphuric acid mono-[2-(3,4-dihydro-isoquinolin-2-yl)-1-(2-butyl-octyloxymethyl)-ethyl] ester, internal salt	0.04	-
N- methyl-3,4-dihydroisoquinolinium p-toluene sulphonate	-	0.04
Nonanoyloxybenzene sulphonate (NOBS)	7.34	7.34
Diethylene Triamine PentaMethylenePhosphate, Na salt	0.9	0.9
Chloride salt of methyl quaternized polyethoxylated hexamethylene diamine	0.95	0.95
Sodium carbonate	3	3
Maleic-acrylic copolymer	3.32	3.32
HEDP-Na salt	0.9	0.9
Protease Prills	0.4	0.4
Amylase Prills	0.84	0.84
Sodium Percarbonate	18.89	18.89
Suds Suppressor	0.35	0.35
Perfume	0.46	0.46
Titanium dioxide	0.5	0.5
Brightener	0.14	0.14
Miscellaneous/Minors	To 100	To 100

Example 3a, 3b and 3c: Dual compartment unit-dose laundry detergent articles of the present invention, encapsulated in a polyvinyl alcohol film, wherein the activated peroxygen source is in a separate compartment from the other laundry ingredients.

Ingredient name	Example 3a	
	Compartment 1	Compartment 2
	32 g	4 g
	WT %	WT %
Linear alkyl benzene sulfonic acid	14.8	--
Phthalimido peroxyacaproic acid (PAP) ⁴	--	33.33
C12-14 alkyl ethoxy 3 sulphate MEA salt	8.8	--
Sulphuric acid mono-[2-(3,4-dihydro-isoquinolin-2-yl)-1-(2-butyl-octyloxymethyl)-ethyl] ester, internal salt	0.04	--
C12-14 alkyl 7-ethoxylate	13.0	--
C12-18 Fatty acid	15.0	--
Enzymes ³	2.3	--
PEG-PVAc polymer	2.0	---
Buffer (Monoethanol amine)	To pH 6.8	--
Solvent	18.6	--
Mineral Oil	--	To 100
Colour	0.008	--
Water	9.5	--
1-Hydroxy Ethylidene-1,1-Diphosphonic Acid (HEDP)	1.2	--
Miscellaneous/Minors	To 100	--

Ingredient name	Example 3b		Example 3c	
	Compartment 1	Compartment 2	Compartment 1	Compartment 2
	32 g	4 g	32 g	4 g
	WT %	WT %	WT %	WT %
Linear alkyl benzene sulfonic acid	26.0	--	27.0	--
Phthalimido peroxyacetic acid (PAP) ³	--	33.33	--	33.33
C12-14 alkyl ethoxy 3 sulphate MEA salt	2.0	--	--	--
Sulphuric acid mono-[2-(3,4-dihydro-isoquinolin-2-yl)-1-(2-butyl-octyloxymethyl)-ethyl] ester, internal salt	0.06	--	--	--
N-methyl-3,4-dihydroisoquinolinium tetrafluoroborate	--	--	0.05	
C12-14 alkyl 7-ethoxylate	15.0	--	20.0	--
C12-18 Fatty acid	18.0	--	20.0	--
Enzymes ²	2.3	--	2.3	--
PEG-PVAc polymer	2.0	---		---
Buffer (Monoethanol amine)	To pH 6.5	--	To pH 8.7	--
Solvent	18.6	--	20.6	--
Mineral Oil	--	To 100	--	To 100
Colour	0.008	--	0.008	--
Water	9.0	--	5.0	--
1-Hydroxy Ethylidene-1,1-Diphosphonic Acid (HEDP)	0.9	--	2.1	--
Miscellaneous/Minors	To 100	--	To 100	--

² Amylase and protease³ Eureco WTM, supplied by Solvay, Aussimont

Example 4: A dual compartment unit-dose laundry detergent article of the present invention, encapsulated in a polyvinyl alcohol film, wherein the activated peroxygen source and the organic catalyst are in separate compartments.

Ingredient name	Compartment 1	Compartment 2
	32 g	7 g
	WT %	WT %
Linear alkyl benzene sulfonic acid	10	14.8
3-(3,4-dihydroisoquinolinium) propane sulfonate, internal salt	--	0.15
Sodium Percarbonate	23	--
Tetraacetyl ethylene diamine (TAED)	5	--
Carbonate	20	--
C12-14 alkyl ethoxy 3 sulphate salt	3	8.8
C12-14 alkyl sulphate salt	2	--
C12-14 alkyl 7-ethoxylate	--	13.0
C12-18 Fatty acid	0	15.0
Enzymes ²	2	2.3
Zeolite	10	--
PEG-PVAc polymer	--	5.0
Monoethanol amine	--	To pH 7.5
Solvent	--	18.6
Colour	--	0.008
Water	--	9.5
Miscellaneous/Minors	To 100	To 100

² Amylase and protease

Example 5a and 5b: Dual compartment unit-dose laundry detergent articles of the present invention, encapsulated in a polyvinyl alcohol film, wherein the activated peroxygen source and the organic catalyst are in separate compartments.

Ingredient name	Example 5a		Example 5b	
	Compartment 1	Compartment 2	Compartment 1	Compartment 2
	32 g	7 g	32 g	7 g
	WT %	WT %	WT %	WT %
Linear alkyl benzene sulfonic acid	10	14.8	10	14.8
Sulphuric acid mono-[2-(3,4-dihydro-isoquinolin-2-yl)-1-(2-butyl-octyloxymethyl)-ethyl] ester, internal salt	--	0.4	--	--
3-(3,4-dihydroisoquinolinium) propane sulfonate, internal salt	--	--	--	0.4
Percarbonate	22	--	22	--
Nonanoyloxybenzene sulphonate (NOBS)	8	--	--	--
4-(isononanoyloxy)benzenesulfonate, sodium salt (iso-NOBS)	--	--	8	--
Sodium Carbonate	20	--	20	--
C12-14 alkyl ethoxy 3 sulphate salt	3	8.8	3	8.8
C12-14 alkyl sulphate salt	2	--	2	--
C12-14 alkyl 7-ethoxylate	--	13.0	--	13.0
C12-18 Fatty acid	0	15.0	0	15.0
Enzymes ²	2	2.3	--	--
Lipase	--	--	2	2.3
Zeolite	10	--	10	--
PEG-PVAc polymer	--	5.0	--	5.0
Monoethanol amine	--	To pH 7.5	--	To pH 7.5
Solvent	--	18.6	--	18.6
Colour	--	0.008	--	0.008
Water	--	9.5	--	9.5
Miscellaneous/Minors	To 100	To 100	To 100	To 100

² Amylase and protease

Example 6: A 3-compartment unit-dose laundry detergent article of the present invention, encapsulated in a polyvinyl alcohol film, wherein the activated peroxygen source, the organic catalyst, and the enzymes, are in separate compartments.

Ingredient name	Compartment 1	Compartment 2	Compartment 3
	30 g	3g	3g
	WT %	WT %	WT %
Linear alkyl benzene sulfonic acid	14.8	--	14.8
Phthalimido peroxyacaproic acid (PAP) ¹	--	33.33	--
Sulphuric acid mono-[2-(3,4-dihydro-isoquinolin-2-yl)-1-(2-butyl-octyloxymethyl)-ethyl] ester, internal salt	0.04	--	
C12-14 alkyl ethoxy 3 sulphate MEA salt	8.8	--	8.8
C12-14 alkyl 7-ethoxylate	13.0	--	13.0
C12-18 Fatty acid	15.0	--	15.0
Enzymes ²	--	--	10
PEG-PVAc polymer	2.0	---	--
Monoethanol amine	To pH 7.5	--	To pH 7.5
Solvent	18.6	--	20
Mineral Oil		To 100	
Colour	0.008	--	0.02
Water	9.5	--	9.5
Miscellaneous/Minors	To 100	--	To 100

² Amylase and protease

Examples 7a and 7b: Dual compartment unit-dose laundry detergent articles of the present invention, encapsulated in a polyvinyl alcohol film, wherein the activated peroxygen source is separated from the other active ingredients.

Ingredient name	Example 7a		Example 7b	
	Compartment 1	Compartment 2	Compartment 1	Compartment 2
	32 g	4 g	32 g	4 g
	WT %	WT %	WT %	WT %
Linear alkyl benzene sulfonic acid	20.5	--	10	--
Caroat ⁴	--	100	--	100
Sulphuric acid mono-[2-(3,4-dihydro-isoquinolin-2-yl)-1-(2-butyl-octyloxymethyl)-ethyl] ester, internal salt	0.06	--	--	--
N-methyl-3,4-dihydroisoquinolinium tetrafluoroborate	--	--	0.04	--
C12-14 alkyl 7-ethoxylate	14.0	--	35.0	--
C12-18 Fatty acid	19.0	--	16.0	--
Enzymes ²	2.3	--	2.3	--
Polymers	2.0	---	2.0	---
Buffer (Monoethanol amine, NaOH)	To pH 7.5	--	To pH 8.5	--
Solvent	18.6	--	18.6	--
Colour	0.008	--	0.008	--
Water	9.5	--	8.5	--
Miscellaneous/Minors	To 100	--	To 100	--

² Amylase and protease

5 ⁴ Caroat (Evonik Industries AG; Rellinghauser Straße 1; 45128 Essen, Germany) – Potassium Peroxymonosulfate

The stability of the aryliminium ion at different pH was evaluated by adjusting the pH of the composition of Example 1a to a pH of 7, 8, and 9 (using either HCl or NaOH), and measuring the
 10 percentage of the aryliminium ion remaining after storage for two weeks at 21°C and also 32°C:

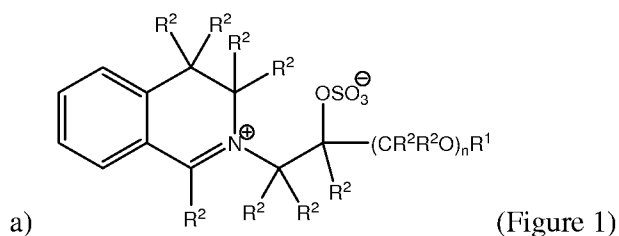
Organic Bleach Catalyst Stability (% Remaining) at 2 weeks		
pH	Storage temp (°C)	% Aryliminium ion remaining
9	21	35
8	21	>95
7	21	>95
9	32	<5
8	32	90
7	32	>95

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”.

CLAIMS

What is claimed is:

- 5 1. A unit dose laundry detergent article comprising:
- a) an anionic and/or nonionic surfactant; and
- b) a bleaching system comprising:
- (i) an organic bleach catalyst consisting of an aryliminium ion selected from the group:
cations, zwitterions, and mixtures thereof; and
- 10 (ii) an activated peroxygen source selected from the group consisting of: a preformed
peracid; a hydrogen peroxide source; and mixtures thereof;
- enclosed in a water-soluble or dispersible film, wherein: at least 50 % by weight of the
anionic and/or nonionic surfactant, and at least 50 % by weight of the aryliminium ions are
comprised in at least one fluid composition.
- 15 2. The unit dose laundry detergent article according to claim 1, wherein the aryliminium ion is a
zwitterion selected from the group consisting of:

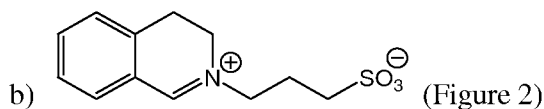


wherein: in Figure 1,

- (i) R^1 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, R^1 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 R^1 is selected from the group consisting of: 2-propylheptyl, 2-butyloctyl, 2-pentylonyl, 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;
- (ii) R^2 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

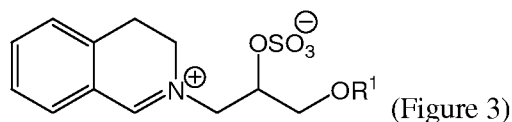
from 1 to 12 carbons; preferably R^2 is independently selected from H and methyl groups;

(iii) n is an integer from 0 to 1;



3-(3,4-dihydroisoquinolinium)propane sulfonate;
and mixtures thereof.

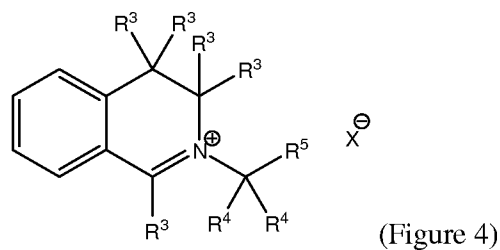
3. The unit dose laundry detergent article according to claim 2, wherein the aryliminium ion is a zwitterion has the structure:



wherein: in Figure 3,

R^1 is a branched alkyl group containing from 9 to 24 carbons or linear alkyl group containing from 11 to 24 carbons, preferably each R^1 is a branched alkyl group containing from 9 to 18 carbons or linear alkyl group containing from 11 to 18 carbons, more preferably each R^1 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.

4. The unit dose laundry detergent article according to claim 1, wherein the aryliminium ion is a cation having the structure:



wherein: in Figure 4,

- (i) R^3 is independently selected from the group consisting of: H and methyl groups; preferably, R^3 is H;
- (ii) R^4 and R^5 are independently selected from the group consisting of: H, a branched alkyl group containing from 3 to 12 carbons, and a linear alkyl group containing from

1 to 12 carbons; preferably, R^4 and R^5 are H or methyl, more preferably, R^4 and R^5 are H;

(iii) X^- is a charge-balancing counterion; preferably a bleach-compatible counterion;

- 5 5. The unit dose laundry detergent article according to any preceding claim, wherein the activated peroxygen source is a preformed peracid selected from the group consisting of: phthalimido peroxycaproic acid (PAP), percarboxylic acids and salts, percarbonic acids and salts, perimidic acids and salts, peroxymonosulphuric acids and salts, and mixtures thereof.
6. The unit dose laundry detergent article according to claim 5, comprising a fluid comprising compartment containing a preformed peracid, having a neat pH of from 4 to 10, preferably
10 from 6.5 to 9, more preferably from 7 to 8.5.
7. The unit dose laundry detergent article according to any preceding claim, wherein the fluid comprising compartment that contains the aryliminium ion has a neat pH of less than 9, preferably less than 8.5, more preferably less than 8, even more preferably less than 7.
8. The unit dose laundry detergent article according to claims 1 to 4, wherein the activated
15 peroxygen source is a hydrogen peroxide source selected from the group consisting of: a peroxide; a persalt; and mixtures thereof.
9. The unit dose laundry detergent article according to claim 8, further comprising a bleach activator.
10. The unit dose laundry detergent article according to claim 9, wherein the bleach activator is
20 selected from the group consisting of: nonanoyloxybenzene sulphonate (NOBS), sodium 4-(isononoyloxy)benzenesulphonate (iso-NOBS), tetraacetyl ethylene diamine (TAED) or mixtures thereof.
11. The unit dose laundry detergent article according to claim 10, wherein the bleach activator is sodium 4-(isononoyloxy)benzenesulphonate (iso-NOBS), and the unit dose laundry
25 detergent article further comprises a lipase enzyme.
12. The unit dose laundry detergent article according to any preceding claim, further comprising perfume microcapsules, wherein the perfume microcapsule wall material preferably comprises: melamine crosslinked with formaldehyde, polyurea, urea crosslinked with formaldehyde, or urea crosslinked with glutaraldehyde.
- 30 13. The unit dose laundry detergent article according to any preceding claim, wherein part of the peroxygen source is physically separated from the aryliminium ions by a means selected from the group consisting of:

- a) at least 50% by weight of the activated peroxygen source being a solid;
- b) at least 50% by weight of the activated peroxygen source being encapsulated by a water-soluble or dispersible barrier; and
- c) at least 50% by weight of the activated peroxygen source being in a different compartment comprising less than 25% by weight of the aryliminium ions.

14. The unit dose laundry detergent article according to any preceding claim, further comprising a deterative enzyme selected from the group consisting of: lipase, protease, amylase, cellulase, pectate lyase, xyloglucanase, and mixtures thereof; wherein at least part of the peroxygen source is physically separated from the deterative enzyme by a means selected from the group consisting of:

- a) at least 50% by weight of the activated peroxygen source being a solid;
- b) at least 50% by weight of the activated peroxygen source being encapsulated by a water-soluble or dispersible barrier; and
- c) at least 50% by weight of the activated peroxygen source being in a different compartment comprising less than 25% by weight of the deterative enzymes.

15. The unit dose laundry detergent article according to any preceding claim, further comprising a perfume; wherein at least part of the peroxygen source is physically separated from the perfume by a means selected from the group consisting of:

- a) at least 50% by weight of the activated peroxygen source being a solid;
- b) at least 50% by weight of the activated peroxygen source being encapsulated by a water-soluble or dispersible barrier; and
- c) at least 50% by weight of the activated peroxygen source being in a different compartment comprising less than 25% by weight of the perfume.

16. A unit dose laundry composition according to any preceding claim, wherein the water-soluble or dispersible film comprises: polyvinyl alcohol, polyvinyl alcohol copolymers, or mixtures thereof

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2011/031312

A. CLASSIFICATION OF SUBJECT MATTER INV. C11D3/39 C11D17/04 C11D1/02 C11D1/66 C11D1/83 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) EP0-Internal, PAJ, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2009/152031 A1 (PROCTER & GAMBLE [US]; BOUTOILLE ALICE MICHELE [BE]; COURCHAY FLORENCE) 17 December 2009 (2009-12-17)	1-3,5-16
Y	example C claim 1 page 3, line 11 - page 7, line 22 page 13, line 2 - line 5 page 22, line 17 - page 23, line 10 -----	1-3,5-16
X	EP 1 496 104 A1 (PROCTER & GAMBLE [US]) 12 January 2005 (2005-01-12)	1-10,12,13,15,16
Y	claims examples I,IX,XIV-XVII page 5, paragraph 51 - paragraph 52 page 7, paragraph 75 - page 8, paragraph 82 page 12, paragraph 122 page 6, paragraph 61 - paragraph 62 ----- -/-	1-10,12,13,15,16
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "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) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "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 invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "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 documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
Date of the actual completion of the international search 27 July 2011		Date of mailing of the international search report 03/08/2011
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Neys, Patricia

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2011/031312

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 01/16274 A1 (PROCTER & GAMBLE [US]; DYKSTRA ROBERT RICHARD [US]; WEED PENNY S [US]) 8 March 2001 (2001-03-08)	1-16
Y	examples IXX,XX Synthesis examples I to IV claims 1-22 page 28, line 21 - page 33, line 2 page 27, line 6 - line 12 page 23, line 25 - page 24, line 25 -----	1-16
X	WO 2007/087242 A2 (PROCTER & GAMBLE [US]; SOUTER PHILIP FRANK [GB]; LANT NEIL JOSEPH [GB]) 2 August 2007 (2007-08-02) claims 1,27-40 examples 6,7,8A-8L page 4, line 5 - line 32 page 17, line 5 - line 23 page 18, line 17 - page 20, line 15 page 21, line 2 - page 23, line 12 -----	1-16
X	EP 1 811 014 A1 (PROCTER & GAMBLE [US]) 25 July 2007 (2007-07-25) the whole document -----	1-16
X	US 2007/197417 A1 (MIRACLE GREGORY S [US]) 23 August 2007 (2007-08-23) the whole document -----	1-3,5-16
X,P	US 2011/005004 A1 (DYKSTRA ROBERT RICHARD [US] ET AL) 13 January 2011 (2011-01-13) examples claims page 2, paragraph 22 - page 4, paragraph 43 -----	1-16
A	WO 01/60966 A1 (PROCTER & GAMBLE [US] PROCTER & GAMBLE [US]; DASQUE BRUNO MATTHIEU [GB]) 23 August 2001 (2001-08-23) examples 11-17 claims page 23, line 35 - page 27, line 12 page 34, line 26 - page 36, line 13 -----	1-16
A	WO 01/85890 A1 (UNILEVER PLC [GB]; UNILEVER NV [NL]; LEVER HINDUSTAN LTD [IN]) 15 November 2001 (2001-11-15) example 5 claims 2,12,13 page 5, line 16 - line 19 -----	4

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2011/031312

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2009152031 A1	17-12-2009	CA 2725687 A1 CN 102119210 A EP 2133410 A1 US 2009312220 A1	17-12-2009 06-07-2011 16-12-2009 17-12-2009
EP 1496104 A1	12-01-2005	AT 394464 T ES 2306838 T3 US 2005008526 A1 WO 2005005590 A1	15-05-2008 16-11-2008 13-01-2005 20-01-2005
WO 0116274 A1	08-03-2001	AR 027846 A1 AT 311432 T AU 7072100 A BR 0014151 A CA 2382023 A1 CN 1384868 A CZ 20020722 A3 DE 60024463 D1 DE 60024463 T2 EG 22867 A EP 1206519 A1 ES 2252054 T3 JP 2003508585 A MA 25602 A1 MX PA02002128 A TR 200200471 T2	16-04-2003 15-12-2005 26-03-2001 07-05-2002 08-03-2001 11-12-2002 16-10-2002 05-01-2006 17-08-2006 30-09-2003 22-05-2002 16-05-2006 04-03-2003 31-12-2002 02-09-2002 21-05-2002
WO 2007087242 A2	02-08-2007	AR 059154 A1 CA 2635927 A1 EP 1979456 A2 JP 2009523900 A	12-03-2008 02-08-2007 15-10-2008 25-06-2009
EP 1811014 A1	25-07-2007	AT 465230 T BR PI0707194 A2 CA 2633695 A1 CN 101370922 A WO 2007083276 A1 JP 2009523853 A US 2007173428 A1 ZA 200805717 A	15-05-2010 26-04-2011 26-07-2007 18-02-2009 26-07-2007 25-06-2009 26-07-2007 25-11-2009
US 2007197417 A1	23-08-2007	NONE	
US 2011005004 A1	13-01-2011	NONE	
WO 0160966 A1	23-08-2001	AR 028508 A1	14-05-2003
WO 0160966 A1		AT 282109 T AU 1807601 A AU 3824001 A BR 0017112 A BR 0108441 A CA 2583037 A1 CA 2583067 A1 CN 1434857 A CN 1401030 A DE 60015716 D1 DE 60015716 T2	15-11-2004 27-08-2001 27-08-2001 14-01-2003 17-12-2002 23-08-2001 23-08-2001 06-08-2003 05-03-2003 16-12-2004 22-12-2005

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2011/031312

Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
		EP 1126070 A1	22-08-2001	
		EP 1255807 A1	13-11-2002	
		ES 2231148 T3	16-05-2005	
		WO 0161099 A1	23-08-2001	

WO 0185890	A1	15-11-2001	AR 033372 A1	17-12-2003
			AT 339493 T	15-10-2006
			AU 7398801 A	20-11-2001
			EP 1280881 A1	05-02-2003
			ZA 200208532 A	22-10-2003
