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(54) Title: METHOD OF TREATING A FABRIC

(57) Abstract: A method of treating a textile in which a textile is contacted with an aqueous solution comprising a nuclease enzyme, preferably a deoxyribonuclease or ribonuclease enzyme and low levels of alkyl benzene sulphonate surfactant, and optionally rinsing and drying the textile.



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## METHOD OF TREATING A FABRIC

## FIELD OF INVENTION

This invention relates to methods of treating textile surfaces.

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## BACKGROUND OF THE INVENTION

Fabric whiteness is a constant challenge for laundry detergent manufacturers. A particular problem can be build up of soils over time. This is problematic for both coloured and white fabrics but may be particularly noticeable on white or pale-coloured fabrics, for example around collars and cuffs where incomplete cleaning occurs. This can also be problematic as it may result in malodour. Many solutions may be considered by the laundry detergent manufacturer based on different cleaning technologies available, such as surfactants, bleaches and enzymes. Many different types of enzyme are available to the detergent formulator for cleaning different types of soils, such as lipases, proteases, amylases, cellulases, peroxygenases, aryl esterases, cutinases, pectinases, mannanases and deoxyribonucleases. Deoxyribonucleases may be particularly effective at cleaning this type of soil, however, in order to provide cleaning, the enzyme needs to deposit on the textile surface. Certain surfactants can reduce this deposition so there is still a need for a cleaning or treatment composition comprising surfactant which enables deposition of the enzyme. The present inventors have found that certain anionic surfactants may be detrimental to the performance of nuclease enzymes but that such surfactants can still be used effectively at low levels of overall surfactant.

## SUMMARY OF THE INVENTION

25 This invention relates to a method of treating a textile comprising (i) contacting the textile with an aqueous solution comprising a nuclease enzyme, preferably a deoxyribonuclease or ribonuclease enzyme and from 0.05g/l to 1g/l of a surfactant system, and from 0 to 0.5g/l sodium aluminosilicate, said surfactant system comprising at least 80% by weight linear alkyl benzene sulphonate surfactant, preferably at least 85 % by weight linear alkyl benzene 30 sulphonate; and optionally rinsing and drying the textile.

Preferably the aqueous solution comprising the nuclease enzyme is provided by the addition of a cleaning composition comprising the nuclease enzyme to water. It may be preferred for the cleaning composition to be in the form of a liquid or a water-soluble unit dose

pouch, preferably a multi-compartment unit dose product, comprising liquid and optionally additionally solid composition.

According to a further aspect of the invention there is provided a cleaning composition as defined herein comprising a nuclease enzyme as defined herein and a glycosyl hydrolase from 5 family GH20, preferably a  $\beta$ -N-acetylglucosaminidase enzyme from E.C. 3.2.1.52.

#### DETAILED DESCRIPTION OF THE INVENTION

##### Definitions

As used herein, the term "alkoxy" is intended to include C1-C8 alkoxy and C1-C8 alkoxy 10 derivatives of polyols having repeating units such as butylene oxide, glycidol oxide, ethylene oxide or propylene oxide.

As used herein, unless otherwise specified, the terms "alkyl" and "alkyl capped" are intended to include C1-C18 alkyl groups, or even C1-C6 alkyl groups.

As used herein, unless otherwise specified, the term "aryl" is intended to include C3-12 15 aryl groups.

As used herein, unless otherwise specified, the term "arylalkyl" and "alkaryl" are equivalent and are each intended to include groups comprising an alkyl moiety bound to an aromatic moiety, typically having C1-C18 alkyl groups and, in one aspect, C1-C6 alkyl groups.

The terms "ethylene oxide," "propylene oxide" and "butylene oxide" may be shown 20 herein by their typical designation of "EO," "PO" and "BO," respectively.

As used herein, the term "cleaning composition" includes, unless otherwise indicated, granular, powder, liquid, gel, paste, unit dose, bar form and/or flake type washing agents and/or fabric treatment compositions, including but not limited to products for laundering fabrics, fabric softening compositions, fabric enhancing compositions, fabric freshening compositions, and 25 other products for the care and maintenance of fabrics, and combinations thereof. Such compositions may be pre-treatment compositions for use prior to a washing step or may be rinse added compositions, as well as cleaning auxiliaries, such as bleach additives and/or "stain-stick" or pre-treat compositions or substrate-laden products such as dryer added sheets.

As used herein, "cellulosic substrates" are intended to include any substrate which 30 comprises cellulose, either 100% by weight cellulose or at least 20% by weight, or at least 30 % by weight or at least 40 or at least 50 % by weight or even at least 60 % by weight cellulose.

Cellulose may be found in wood, cotton, linen, jute, and hemp. Cellulosic substrates may be in the form of powders, fibers, pulp and articles formed from powders, fibers and pulp. Cellulosic fibers, include, without limitation, cotton, rayon (regenerated cellulose), acetate (cellulose

acetate), triacetate (cellulose triacetate), and mixtures thereof. Typically cellulosic substrates comprise cotton. Articles formed from cellulosic fibers include textile articles such as fabrics. Articles formed from pulp include paper.

As used herein, the term “maximum extinction coefficient” is intended to describe the 5 molar extinction coefficient at the wavelength of maximum absorption (also referred to herein as the maximum wavelength), in the range of 400 nanometers to 750 nanometers.

As used herein “average molecular weight” is reported as an average molecular weight, as determined by its molecular weight distribution: as a consequence of their manufacturing process, polymers disclosed herein may contain a distribution of repeating units in their 10 polymeric moiety.

As used herein the term "variant" refers to a polypeptide that contains an amino acid sequence that differs from a wild type or reference sequence. A variant polypeptide can differ from the wild type or reference sequence due to a deletion, insertion, or substitution of a nucleotide(s) relative to said reference or wild type nucleotide sequence. The reference or wild 15 type sequence can be a full-length native polypeptide sequence or any other fragment of a full-length polypeptide sequence. A polypeptide variant generally has at least about 70% amino acid sequence identity with the reference sequence, but may include 75% amino acid sequence identity within the reference sequence, 80% amino acid sequence identity within the reference sequence, 85% amino acid sequence identity with the reference sequence, 86% amino acid 20 sequence identity with the reference sequence, 87% amino acid sequence identity with the reference sequence, 88% amino acid sequence identity with the reference sequence, 89% amino acid sequence identity with the reference sequence, 90% amino acid sequence identity with the reference sequence, 91% amino acid sequence identity with the reference sequence, 92% amino acid sequence identity with the reference sequence, 93% amino acid sequence identity with the reference sequence, 95% amino 25 sequence identity with the reference sequence, 96% amino acid sequence identity with the reference sequence, 97% amino acid sequence identity with the reference sequence, 98% amino acid sequence identity with the reference sequence, 98.5% amino acid sequence identity with the reference sequence or 99% amino acid sequence identity with the reference sequence.

As used herein, articles such as “a” and “an” when used in a claim, are understood to 30 mean one or more of what is claimed or described.

As used herein, the terms “include/s” and “including” are meant to be non-limiting.

As used herein, the term “solid” includes granular, powder, bar and tablet product forms.

As used herein, the term “fluid” includes liquid, gel, paste and gas product forms.

Unless otherwise noted, all component or composition levels are in reference to the active portion of that component or composition, and are exclusive of impurities, for example, residual solvents or by-products, which may be present in commercially available sources of such components or compositions.

5 All percentages and ratios are calculated by weight unless otherwise indicated. All percentages and ratios are calculated based on the total composition unless otherwise indicated.

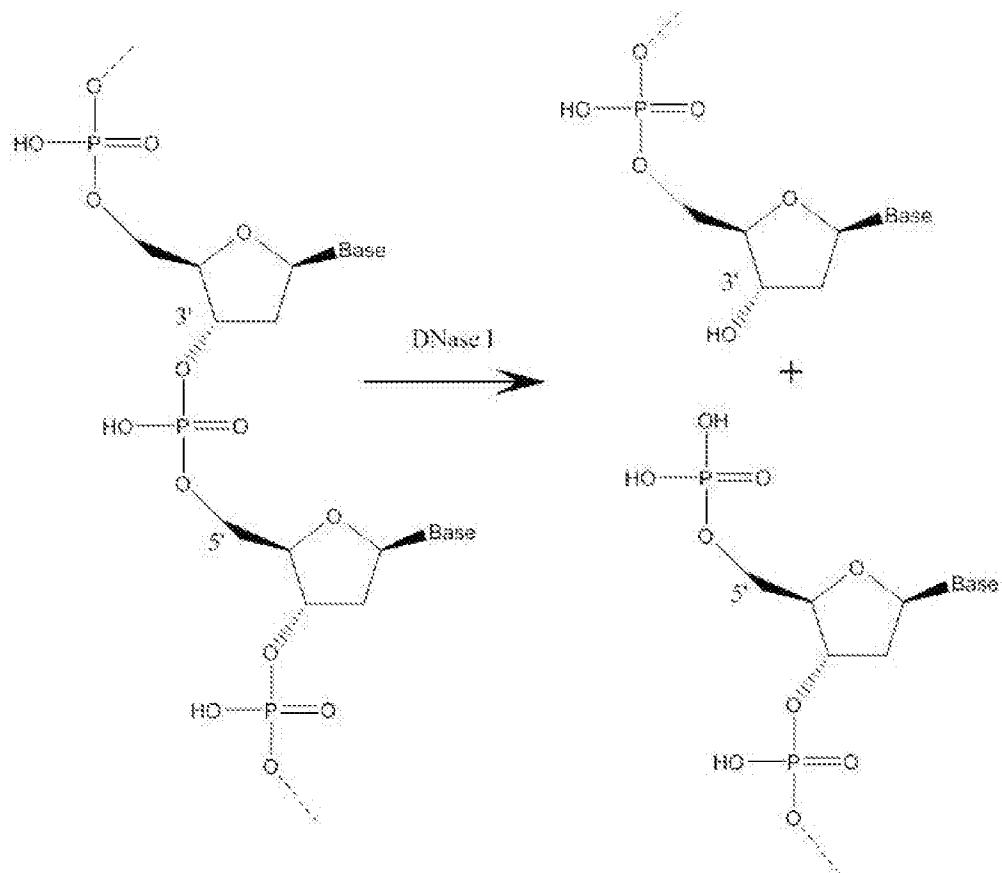
The textile is contacted with an aqueous solution comprising a nuclease enzyme and a surfactant system and optionally sodium aluminosilicate. The nuclease enzyme and surfactant system are preferably provided as a cleaning composition for adding to water to form the 10 aqueous solution. The aqueous solution also additionally comprises surfactant, preferably in an amount from 0.05 g/l to 1 g/l of surfactant or from 0.1 to 0.9 g/l or to 0.8 or even 0.6g/l. Preferably the aqueous solution comprises the wash water in a laundering step either hand wash or by machine, most preferably in an automatic washing machine. The cleaning composition will comprise in addition to the nuclease enzyme and surfactant system, additional adjunct 15 materials from such a cleaning composition, as described below.

#### Nuclease Enzyme

The nuclease enzyme is an enzyme capable of cleaving the phosphodiester bonds between the nucleotide sub-units of nucleic acids. The nuclease enzyme herein is preferably a deoxyribonuclease or ribonuclease enzyme or a functional fragment thereof. By functional 20 fragment or part is meant the portion of the nuclease enzyme that catalyzes the cleavage of phosphodiester linkages in the DNA backbone and so is a region of said nuclease protein that retains catalytic activity. Thus it includes truncated, but functional versions, of the enzyme and/or variants and/or derivatives and/or homologues whose functionality is maintained.

Preferably the nuclease enzyme is a deoxyribonuclease, preferably selected from any of 25 the classes E.C. 3.1.21.x, where x=1, 2, 3, 4, 5, 6, 7, 8 or 9, E.C. 3.1.22.y where y=1, 2, 4 or 5, E.C. 3.1.30.z where z= 1 or 2, E.C. 3.1.31.1 and mixtures thereof.

Nucleases in class E.C. 3.1.21.x cleave at the 3' hydroxyl to liberate 5' phosphomonoesters as follows:



Nuclease enzymes from class E.C. 3.1.21.x and especially where x=1 are particularly preferred.

5 Nucleases in class E.C. 3.1.22.y cleave at the 5' hydroxyl to liberate 3' phosphomonoesters. Enzymes in class E.C. 3.1.30.z may be preferred as they act on both DNA and RNA and liberate 5'-phosphomonoesters. Suitable examples from class E.C. 3.1.31.2 are described in US2012/0135498A, such as SEQ ID NO:3 therein. Such enzymes are commercially available as DENARASE® enzyme from c-LECTA.

10 Nuclease enzymes from class E.C. 3.1.31.1 produce 3'phosphomonoesters.

Preferably, the nuclease enzyme comprises a microbial enzyme. The nuclease enzyme may be fungal or bacterial in origin. Bacterial nucleases may be most preferred. Fungal nucleases may be most preferred.

15 The microbial nuclease is obtainable from *Bacillus*, such as a *Bacillus licheniformis* or *Bacillus subtilis* bacterial nucleases. A preferred nuclease is obtainable from *Bacillus licheniformis*, preferably from strain EI-34-6. A preferred deoxyribonuclease is a variant of *Bacillus licheniformis*, from strain EI-34-6 nucB deoxyribonuclease defined in SEQ ID NO:1

herein, or variant thereof, for example having at least 70% or 75% or 80% or 85% or 90% or 95%, 96%, 97%, 98%, 99% or 100% identical thereto.

Other suitable nucleases are defined in SEQ ID NO:2 herein, or variant thereof, for example having at least 70% or 75% or 80% or 85% or 90% or 95%, 96%, 97%, 98%, 99% or 100% identical thereto. Other suitable nucleases are defined in SEQ ID NO:3 herein, or variant thereof, for example having at least 70% or 75% or 80% or 85% or 90% or 95%, 96%, 97%, 98%, 99% or 100% identical thereto.

A fungal nuclease is obtainable from *Aspergillus*, for example *Aspergillus oryzae*. A preferred nuclease is obtainable from *Aspergillus oryzae* defined in SEQ ID NO: 5 herein, or variant thereof, for example having at least 60% or 70% or 75% or 80% or 85% or 90% or 95%, 96%, 97%, 98%, 99% or 100% identical thereto.

Another suitable fungal nuclease is obtainable from *Trichoderma*, for example *Trichoderma harzianum*. A preferred nuclease is obtainable from *Trichoderma harzianum* defined in SEQ ID NO: 6 herein, or variant thereof, for example having at least 60% or 70% or 75% or 80% or 85% or 90% or 95%, 96%, 97%, 98%, 99% or 100% identical thereto.

Other fungal nucleases include those encoded by the DNA sequences of *Aspergillus oryzae* RIB40, *Aspergillus oryzae* 3.042, *Aspergillus flavus* NRRL3357, *Aspergillus parasiticus* SU-1, *Aspergillus nomius* NRRL13137, *Trichoderma reesei* QM6a, *Trichoderma virens* Gv29-8, *Oidiodendron maius* Zn, *Metarhizium guizhouense* ARSEF 977, *Metarhizium majus* ARSEF 297, *Metarhizium robertsii* ARSEF 23, *Metarhizium acridum* CQM1 102, *Metarhizium brunneum* ARSEF 3297, *Metarhizium anisopliae*, *Colletotrichum fioriniae* PJ7, *Colletotrichum sublineola*, *Trichoderma atroviride* IMI 206040, *Tolypocladium ophioglossoides* CBS 100239, *Beauveria bassiana* ARSEF 2860, *Colletotrichum higginsianum*, *Hirsutella minnesotensis* 3608, *Scedosporium apiospermum*, *Phaeomoniella chlamydospora*, *Fusarium verticillioides* 7600, *Fusarium oxysporum* f. sp. *cubense* race 4, *Colletotrichum graminicola* M1.001, *Fusarium oxysporum* FOSC 3-a, *Fusarium avenaceum*, *Fusarium langsethiae*, *Grosmannia clavigera* kw1407, *Claviceps purpurea* 20.1, *Verticillium longisporum*, *Fusarium oxysporum* f. sp. *cubense* race 1, *Magnaporthe oryzae* 70-15, *Beauveria bassiana* D1-5, *Fusarium pseudograminearum* CS3096, *Neonectria ditissima*, *Magnaportheopsis poae* ATCC 64411, *Cordyceps militaris* CM01, *Marssonina brunnea* f. sp. 'multigermtubi' MB\_m1, *Diaporthe ampelina*, *Metarhizium album* ARSEF 1941, *Colletotrichum gloeosporioides* Nara gc5, *Madurella mycetomatis*, *Metarhizium brunneum* ARSEF 3297, *Verticillium alfalfae* VaMs.102, *Gaeumannomyces graminis* var. *tritici* R3-111a-1, *Nectria haematococca* mpVI 77-13-4, *Verticillium longisporum*, *Verticillium dahliae* VdLs.17, *Torrubiella hemipterigena*,

*Verticillium longisporum*, *Verticillium dahliae* VdLs.17, *Botrytis cinerea* B05.10, *Chaetomium globosum* CBS 148.51, *Metarhizium anisopliae*, *Stemphylium lycopersici*, *Sclerotinia borealis* F-4157, *Metarhizium robertsii* ARSEF 23, *Mycelophtora thermophila* ATCC 42464,

*Phaeosphaeria nodorum* SN15, *Phialophora attae*, *Ustilaginoides virens*, *Diplodia seriata*,

5 *Ophiostoma piceae* UAMH 11346, *Pseudogymnoascus pannorum* VKM F-4515 (FW-2607), *Bipolaris oryzae* ATCC 44560, *Metarhizium guizhouense* ARSEF 977, *Chaetomium thermophilum* var. *thermophilum* DSM 1495, *Pestalotiopsis fici* W106-1, *Bipolaris zeicola* 26-R-13, *Setosphaeria turcica* Et28A, *Arthroderma otae* CBS 113480 and *Pyrenophora tritici-repentis* Pt-1C-BFP.

10 Preferably the nuclease is an isolated nuclease.

Preferably the nuclease enzyme is present in the aqueous solution in an amount of from 0.01ppm to 1000 ppm of the nuclease enzyme, or from 0.05 or from 0.1ppm to 750 or 500ppm.

The nucleases may also give rise to biofilm-disrupting effects.

#### Surfactant System

15 The surfactant system comprises at least 80% by weight linear alkyl benzene sulphonate surfactant, preferably at least 85 % by weight alkyl benzene sulphonate (LAS), or even at least 87 or at least 90 wt% based on the total weight of surfactant.

Preferred alkyl benzene sulphonates are linear. Preferred alkyl sulphonates are selected from C<sub>10-13</sub> alkyl benzene sulphonates. Suitable alkyl benzene sulphonate (LAS) may be obtained, by sulphonating commercially available linear alkyl benzene (LAB); suitable LAB includes low 2-phenyl LAB, such as those supplied by Sasol under the tradename Isochem® or those supplied by Petresa under the tradename Petrelab®, other suitable LAB include high 2-phenyl LAB, such as those supplied by Sasol under the tradename Hyblene®. A suitable anionic detergents surfactant is alkyl benzene sulphonate that is obtained by DETAL catalyzed process, although other synthesis routes, such as HF, may also be suitable. In one aspect a magnesium salt of LAS is used.

The surfactant system may comprise additional surfactants which can be selected from nonionic, non-LAS anionic, cationic, amphoteric, ampholytic, amphiphilic, zwitterionic, semi-polar nonionic surfactants and mixtures thereof. Preferred compositions comprise a mixture of surfactants, however the LAS must be present in amounts at least 80 wt% of the surfactant system. Preferred surfactant systems comprise one or more anionic surfactants, most preferably in combination with a co-surfactant, most preferably a nonionic and/or amphoteric and/or zwitterionic surfactant. Preferred surfactant systems comprise both anionic and nonionic surfactant. When present, the total surfactant level in the cleaning composition is preferably

from 0.1% to 60%, from 1% to 50% or even from 5% to 40% by weight of the cleaning composition.

Suitable anionic co-surfactants may be selected from optionally alkoxylated sulphates. Preferred sulphate detergents include alkyl sulphate, typically C<sub>8-18</sub> alkyl sulphate, or 5 predominantly C<sub>12</sub> alkyl sulphate. A further preferred alkyl sulphate is alkyl alkoxylated sulphate, preferably a C<sub>8-18</sub> alkyl alkoxylated sulphate. Preferably the alkoxylating group is an ethoxylating group. Typically the alkyl alkoxylated sulphate has an average degree of alkoxylation of from 0.5 to 30 or 20, or from 0.5 to 10. Particularly preferred are C<sub>8-18</sub> alkyl ethoxylated sulphate having an average degree of ethoxylation of from 0.5 to 10, from 0.5 to 7, 10 from 0.5 to 5 or even from 0.5 to 3.

The alkyl sulphate, alkyl alkoxylated sulphate and alkyl benzene sulphonates may be linear or branched, substituted or un-substituted. When the surfactant is branched, preferably the surfactant will comprise a mid-chain branched sulphate or sulphonate surfactant. Preferably the branching groups comprise C<sub>1-4</sub> alkyl groups, typically methyl and/or ethyl groups.

15 Preferably the composition comprises a nonionic detergents surfactant. Suitable non-ionic surfactants are selected from the group consisting of: C<sub>8-C<sub>18</sub></sub> alkyl ethoxylates, such as, NEODOL® non-ionic surfactants from Shell; C<sub>6-C<sub>12</sub></sub> alkyl phenol alkoxylates wherein the alkoxylate units may be ethyleneoxy units, propyleneoxy units or a mixture thereof; C<sub>12-C<sub>18</sub></sub> alcohol and C<sub>6-C<sub>12</sub></sub> alkyl phenol condensates with ethylene oxide/propylene oxide block 20 polymers such as Pluronic® from BASF; C<sub>14-C<sub>22</sub></sub> mid-chain branched alcohols; C<sub>14-C<sub>22</sub></sub> mid-chain branched alkyl alkoxylates, typically having an average degree of alkoxylation of from 1 to 30; alkylpolysaccharides, in one aspect, alkylpolyglycosides; polyhydroxy fatty acid amides; ether capped poly(oxyalkylated) alcohol surfactants; and mixtures thereof.

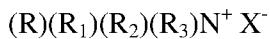
25 Suitable non-ionic detergents surfactants include alkyl polyglucoside and/or an alkyl alkoxylated alcohol.

In one aspect, non-ionic detergents surfactants include alkyl alkoxylated alcohols, in one aspect C<sub>8-18</sub> alkyl alkoxylated alcohol, for example a C<sub>8-18</sub> alkyl ethoxylated alcohol, the alkyl alkoxylated alcohol may have an average degree of alkoxylation of from 1 to 80, preferably from 1 to 50, most preferably from 1 to 30, from 1 to 20, or from 1 to 10. In one aspect, the alkyl 30 alkoxylated alcohol may be a C<sub>8-18</sub> alkyl ethoxylated alcohol having an average degree of ethoxylation of from 1 to 10, from 1 to 7, more from 1 to 5 or from 3 to 7, or even below 3 or 2. The alkyl alkoxylated alcohol can be linear or branched, and substituted or un-substituted.

Suitable nonionic surfactants include those with the tradename Lutensol® ( BASF).

Suitable cationic detergents include alkyl pyridinium compounds, alkyl quaternary ammonium compounds, alkyl quaternary phosphonium compounds, alkyl ternary sulphonium compounds, and mixtures thereof.

Suitable cationic detergents are quaternary ammonium compounds having the general formula:



wherein, R is a linear or branched, substituted or unsubstituted C<sub>6-18</sub> alkyl or alkenyl moiety, R<sub>1</sub> and R<sub>2</sub> are independently selected from methyl or ethyl moieties, R<sub>3</sub> is a hydroxyl, hydroxymethyl or a hydroxyethyl moiety, X is an anion which provides charge neutrality, suitable anions include: halides, for example chloride; sulphate; and sulphonate. Suitable cationic detergents are mono-C<sub>6-18</sub> alkyl mono-hydroxyethyl di-methyl quaternary ammonium chlorides. Highly suitable cationic detergents are mono-C<sub>8-10</sub> alkyl mono-hydroxyethyl di-methyl quaternary ammonium chloride, mono-C<sub>10-12</sub> alkyl mono-hydroxyethyl di-methyl quaternary ammonium chloride and mono-C<sub>10</sub> alkyl mono-hydroxyethyl di-methyl quaternary ammonium chloride.

Suitable amphoteric/zwitterionic surfactants include amine oxides and betaines.

Amine-neutralized anionic surfactants - Anionic surfactants of the present invention and adjunct anionic cosurfactants, may exist in an acid form, and said acid form may be neutralized to form a surfactant salt which is desirable for use in the present detergent compositions. Typical agents for neutralization include the metal counterion base such as hydroxides, eg, NaOH or KOH. Further preferred agents for neutralizing anionic surfactants of the present invention and adjunct anionic surfactants or cosurfactants in their acid forms include ammonia, amines, or alkanolamines. Alkanolamines are preferred. Suitable non-limiting examples including monoethanolamine, diethanolamine, triethanolamine, and other linear or branched alkanolamines known in the art; for example, highly preferred alkanolamines include 2-amino-1-propanol, 1-aminopropanol, monoisopropanolamine, or 1-amino-3-propanol. Amine neutralization may be done to a full or partial extent, e.g. part of the anionic surfactant mix may be neutralized with sodium or potassium and part of the anionic surfactant mix may be neutralized with amines or alkanolamines.

In a preferred composition, the composition additionally comprises a  $\beta$ -N-acetylglucosaminidase enzyme from E.C. 3.2.1.52, preferably an enzyme having at least 70%, or at least 75% or at least 80% or at least 85% or at least 90% or at least 95% or at least 96% or at least 97% or at least 98% or at least 99% or at least or 100% identity to SEQ ID NO:4.

#### Sodium Aluminosilicate

The level of sodium aluminosilicate present in the aqueous liquor is from 0 to 0.5g/l sodium aluminosilicate (anhydrous basis). More preferably the level of sodium aluminosilicate is from 0 to 0.4g/l, or below 0.3g/l, or below 0.2g/l or below 0.1g/l or below 0.05g/l.

Cleaning Adjunct Materials

5 When the aqueous solution is provided by the addition of a cleaning composition to water, in addition to the nuclease enzyme the cleaning composition will comprise optional cleaning and/or treatment adjunct materials. The nuclease enzyme will preferably be present in the composition in amounts of 0.00001% to about 3% by weight, from about 0.0001% to about 2% by weight or even from about 0.001% to about 1% by weight enzyme protein by weight of  
10 the composition.

Preferably the composition will additionally comprise a  $\beta$ -N-acetylglucosaminidase enzyme from E.C. 3.2.1.52, preferably an enzyme having at least 70%, or at least 75% or at least 80% or at least 85% or at least 90% or at least 95% or at least 96% or at least 97% or at least 98% or at least 99% or at least or 100% identity to SEQ ID NO: 4. When present, the  $\beta$ -N-acetylglucosaminidase enzyme will typically be present in an amount from 0.00001% to about 2%, from about 0.0001% to about 1% or even from about 0.001% to about 0.5% enzyme protein by weight of the composition.

Further suitable adjuncts may be, for example to assist or enhance cleaning performance, for treatment of the substrate to be cleaned, for example by softening or freshening, or to modify 20 the aesthetics of the detergent composition as is the case with perfumes, colorants, non-fabric-shading dyes or the like. Suitable adjunct materials include, but are not limited to, surfactants, builders, chelating agents, dispersants, enzymes, and enzyme stabilizers, catalytic materials, bleach activators, hydrogen peroxide, sources of hydrogen peroxide, preformed peracids, polymeric dispersing agents, clay soil removal/anti-redeposition agents, additional brighteners, 25 suds suppressors, dyes, hueing dyes, perfumes, perfume delivery systems, structure elasticizing agents, fabric softeners, carriers, hydrotropes, processing aids, solvents, additional dyes and/or pigments, some of which are discussed in more detail below. In addition to the disclosure below, suitable examples of such other adjuncts and levels of use are found in U.S. Patent Nos. 5,576,282, 6,306,812 B1 and 6,326,348 B1 that are incorporated by reference.

30 Particularly preferred additional adjunct materials may be further enzymes.

**Enzymes.** Preferably the composition comprises one or more additional enzymes. Preferred enzymes provide cleaning performance and/or fabric care benefits. Examples of suitable enzymes include, but are not limited to, hemicellulases, peroxidases, proteases, cellulases, xylanases, lipases, phospholipases, esterases, cutinases, pectinases, mannanases,

pectate lyases, keratinases, reductases, oxidases, phenoloxidases, lipoxygenases, ligninases, pullulanases, tannases, pentosanases, malanases,  $\beta$ -glucanases, arabinosidases, hyaluronidase, chondroitinase, laccase, and amylases, or mixtures thereof. A preferred combination of additional enzymes comprises a protease and a lipase, preferably in conjunction with amylase.

5 When present in the composition, the aforementioned additional enzymes may each be present at levels from about 0.00001% to about 2%, from about 0.0001% to about 1% or even from about 0.001% to about 0.5% enzyme protein by weight of the composition.

**Proteases.** Preferably the composition comprises one or more proteases. Suitable proteases include metalloproteases and 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 lenthus*, *B. alkalophilus*, *B. subtilis*, *B. amyloliquefaciens*, *Bacillus pumilus* and *Bacillus gibsonii* described in US 6,312,936 B1, US 5,679,630, US 4,760,025, US7,262,042 and WO09/021867.

20 (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 07/044993A2.

25 Preferred proteases include those derived from *Bacillus gibsonii* or *Bacillus Lenthus*.

Suitable commercially available protease enzymes include those sold under the trade names Alcalase®, Savinase®, Primase®, Durazym®, Polarzyme®, Kannase®, 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 following 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, or as disclosed in WO2009/149144, WO2009/149145, WO2010/56653, WO2010/56640,

5 WO2011/072117, US2011/0237487, WO2011/140316, WO2012/151480, EP2510092, EP2566960 OR EP2705145.

**Amylases.** Preferably the composition may comprise an amylase. Suitable alpha-amylases include those of bacterial or fungal origin. Chemically or genetically modified mutants (variants) are included. A preferred alkaline alpha-amylase is derived from a strain of *Bacillus*, 10 such as *Bacillus licheniformis*, *Bacillus amyloliquefaciens*, *Bacillus stearothermophilus*, *Bacillus subtilis*, or other *Bacillus* sp., such as *Bacillus* sp. NCIB 12289, NCIB 12512, NCIB 12513, DSM 9375 (USP 7,153,818) DSM 12368, DSMZ no. 12649, KSM AP1378 (WO 97/00324), KSM K36 or KSM K38 (EP 1,022,334). Preferred amylases include:

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

(b) the variants described in USP 5,856,164 and WO99/23211, WO 96/23873, WO00/60060 and WO 06/002643, especially the variants with one or more substitutions in the 20 following positions versus the AA560 enzyme listed as SEQ ID No. 12 in WO 06/002643:

26, 30, 33, 82, 37, 106, 118, 128, 133, 149, 150, 160, 178, 182, 186, 193, 203, 214, 231, 256, 257, 258, 269, 270, 272, 283, 295, 296, 298, 299, 303, 304, 305, 311, 314, 315, 318, 319, 339, 345, 361, 378, 383, 419, 421, 437, 441, 444, 445, 446, 447, 450, 461, 471, 482, 484, preferably that also contain the deletions of D183\* and G184\*.

25 (c) variants exhibiting at least 90% identity with SEQ ID No. 4 in WO06/002643, the wild-type enzyme from *Bacillus* SP722, especially variants with deletions in the 183 and 184 positions and variants described in WO 00/60060, which is incorporated herein by reference.

(d) variants exhibiting at least 95% identity with the wild-type enzyme from *Bacillus* sp.707 (SEQ ID NO:7 in US 6,093, 562), especially those comprising one or more of the 30 following mutations M202, M208, S255, R172, and/or M261. Preferably said amylase comprises one or more of M202L, M202V, M202S, M202T, M202I, M202Q, M202W, S255N and/or R172Q. Particularly preferred are those comprising the M202L or M202T mutations.

(e) variants described in WO 09/149130, preferably those exhibiting at least 90% identity with SEQ ID NO: 1 or SEQ ID NO:2 in WO 09/149130, the wild-type enzyme from *Geobacillus Stearothermophilus* or a truncated version thereof;

5 (f) variants as described in EP2540825 and EP2357220, EP2534233; (g) variants as described in WO2009100102 and WO2010115028.

Suitable commercially available alpha-amylases include DURAMYL®, LIQUEZYME®, TERMAMYL®, TERMAMYL ULTRA®, NATALASE®, SUPRAMYL®, STAINZYME®, STAINZYME PLUS®, FUNGAMYL® and BAN® (Novozymes A/S, Bagsvaerd, Denmark), KEMZYM® AT 9000 Biozym Biotech Trading GmbH Wehlistrasse 27b A-1200 Wien Austria, 10 RAPIDASE®, PURASTAR®, ENZYSIZE®, OPTISIZE HT PLUS®, POWERASE® and PURASTAR OXAM® (Genencor International Inc., Palo Alto, California) and KAM® (Kao, 14-10 Nihonbashi Kayabacho, 1-chome, Chuo-ku Tokyo 103-8210, Japan). In one aspect, suitable amylases include NATALASE®, STAINZYME® and STAINZYME PLUS® and mixtures thereof.

15 **Lipases.** Preferably the composition comprises one or more lipases, including “first cycle lipases” such as those described in U.S. Patent 6,939,702 B1 and US PA 2009/0217464. Preferred lipases are first-wash lipases. In one embodiment of the invention the composition comprises a first wash lipase. First wash lipases includes a lipase which is a polypeptide having an amino acid sequence which: (a) has at least 90% identity with the wild-type lipase derived 20 from *Humicola lanuginosa* strain DSM 4109; (b) compared to said wild-type lipase, comprises a substitution of an electrically neutral or negatively charged amino acid at the surface of the three-dimensional structure within 15A of E1 or Q249 with a positively charged amino acid; and (c) comprises a peptide addition at the C-terminal; and/or (d) comprises a peptide addition at the N-terminal and/or (e) meets the following limitations: i) comprises a negative amino acid in 25 position E210 of said wild-type lipase; ii) comprises a negatively charged amino acid in the region corresponding to positions 90-101 of said wild-type lipase; and iii) comprises a neutral or negative amino acid at a position corresponding to N94 or said wild-type lipase and/or has a negative or neutral net electric charge in the region corresponding to positions 90-101 of said wild-type lipase. Preferred are variants of the wild-type lipase from *Thermomyces lanuginosus* 30 comprising one or more of the T231R and N233R mutations. The wild-type sequence is the 269 amino acids (amino acids 23 – 291) of the Swissprot accession number Swiss-Prot O59952 (derived from *Thermomyces lanuginosus* (*Humicola lanuginosa*)). Preferred lipases would include those sold under the tradenames Lipex® and Lipolex® and Lipoclean®. Other suitable lipases include those described in European Patent Application No. 12001034.3 or EP2623586.

**Endoglucanases.** Other preferred enzymes 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 US7,141,403B2) and mixtures thereof. Suitable endoglucanases are sold under the tradenames Celluclean® and Whitezyme® (Novozymes A/S, Bagsvaerd, Denmark).

**Pectate Lyases.** Other preferred enzymes include pectate lyases sold under the tradenames Pectawash®, Pectaway®, Xpect® and mannanases sold under the tradenames Mannaway® (all from Novozymes A/S, Bagsvaerd, Denmark), and Purabrite® (Genencor International Inc., Palo Alto, California).

**Antimicrobials.** It may be preferred for the compositions to comprise in addition, one or mixtures of more than one compounds which may give rise to anti-microbial effects. These may be standard ingredients of the treatment compositions that are added for cleaning or malodor benefits such as bleaching agents, but have some anti-microbial effect or they may be added specifically to provide anti-microbial effect. Suitable examples may include but are not limited to aldehydes (formaldehyde, glutaraldehyde, ortho-phtalaldehyde), sulphur dioxide, sulphites, bisulphites, vanillic acid esters), chlorine and oxygen based oxidizing agents (sodium and calcium hypochlorite or hypobromite, chloramine and chloramine-T, chlorine dioxide, hydrogen peroxide, iodine, ozone, peracetic acid, performic acid, potassium permanganate, potassium peroxyomonosulfate), phenolics (phenol, o-phenylphenol, chloroxylenol, hexachlorophene, thymol, amylnetacresol, 2,4-dichlorobenzyl alcohol, policresylen, fentichlor, 4-allylcatechol, p-hydroxybenzoic acid esters including benzylparaben, butylparaben, ethylparaben, methylparaben and propylparaben, butylated hydroxyanisole, butylated hydroxytoluene, capaicin, carvacrol, creosol, eugenol, guaiacol), halogenated (hydroxy)diphenylethers (diclosan, triclosan, hexachlorophene and bromochlorophene, 4-hexylresorcinol, 8-hydroxyquinoline and salts thereof), quaternary ammonium compounds (benzalkonium chloride derivatives, benzethonium chloride derivatives, cetrimonium chloride/bromide, cetylpyridinium, cetrimide, benzoxonium chloride, didecyldimethyl ammonium chloride), acridine derivatives (ethacridine lactate, 9-aminoacridine, euflavine), biguanides including polymeric biguanides, and amidines (polyaminopropyl biguanide, dibromopropamidine, chlorhexidine, alexidine, propamidine, hexamidine, polihexanide), nitrofuran derivatives (nitrofurazone), quinoline derivatives (dequalinium, chlorquinadol, oxyquinoline, clioquinol), iodine products, essential oils (bay, cinnamon, clove, thyme, eucalyptus, peppermint, lemon, tea tree, magnolia extract, menthol, geraniol), cations, Anilides (saclylanilide, Diphenylureas), salicylic acid esters including

menthyl salicylate, methyl salicylate and phenyl salicylate, pyrocatechol, phtalic acid and salts thereof, hexetidine, octenidine, sanguinarine, domiphen bromide, alkylpyridinium chlorides such as cetylpyridinium chloride, tetradecylpyridinium chloride and N-tetradecyl-4-ethylpyridinium chloride, iodine, sulfonamides, piperidino derivatives such as delmopinol and octapinol, and mixtures thereof, miscellaneous preservatives (derivatives of 1,3-dioxane, derivatives of imidazole, Isothizolones, derivatives of hexamine, triazines, oxazolo-oxazoles, sodium hydroxymethylglycinate, methylene bisthiocyanate, captan).

Preferred antibacterial systems are halogenated benzyl alcohol derivatives such as chloroxylenol (PCMX), halogenated hydroxydiphenylethers preferably diclosan, quaternary ammonium salts preferably alkylbenzalkonium and alkylbenzethonium chloride and derivatives thereof, essential oils, bleach system preferably a peroxide bleach, and mixtures thereof. Most preferred antibacterial systems are benzalkonium chloride, diclosan and PCMX.

**Encapsulates.** The composition may comprise an encapsulate, for example an encapsulate comprising a core, a shell having an inner and outer surface, said shell encapsulating said core. The core may comprise any laundry care adjunct, though typically the core may comprise material selected from the group consisting of perfumes; brighteners; dyes; insect repellants; silicones; waxes; flavors; vitamins; fabric softening agents; skin care agents in one aspect, paraffins; enzymes; anti-bacterial agents; bleaches; sensates; and mixtures thereof; and said shell may comprise a material selected from the group consisting of polyethylenes; polyamides; polyvinylalcohols, optionally containing other co-monomers; polystyrenes; polyisoprenes; polycarbonates; polyesters; polyacrylates; aminoplasts, in one aspect said aminoplast may comprise a polyureas, polyurethane, and/or polyureaurethane, in one aspect said polyurea may comprise polyoxymethyleneurea and/or melamine formaldehyde; polyolefins; polysaccharides, in one aspect said polysaccharide may comprise alginate and/or chitosan; gelatin; shellac; epoxy resins; vinyl polymers; water insoluble inorganics; silicone; and mixtures thereof. Preferred encapsulates comprise perfume. Preferred encapsulates comprise a shell which may comprise melamine formaldehyde and/or cross linked melamine formaldehyde. Preferred encapsulates comprise a core material and a shell, said shell at least partially surrounding said core material, is disclosed. At least 75%, 85% or even 90% of said encapsulates may have a fracture strength of from 0.2 MPa to 10 MPa, and a benefit agent leakage of from 0% to 20%, or even less than 10% or 5% based on total initial encapsulated benefit agent. Preferred are those in which at least 75%, 85% or even 90% of said encapsulates may have (i) a particle size of from 1 microns to 80 microns, 5 microns to 60 microns, from 10 microns to 50 microns, or even from 15 microns to 40 microns, and/or (ii) at least 75%, 85% or

even 90% of said encapsulates may have a particle wall thickness of from 30 nm to 250 nm, from 80 nm to 180 nm, or even from 100 nm to 160 nm. Formaldehyde scavengers may be employed with the encapsulates, for example, in a capsule slurry and/or added to a composition before, during or after the encapsulates are added to such composition. Suitable capsules that  
5 can be made by following the teaching of USPA 2008/0305982 A1; and/or USPA 2009/0247449 A1. Alternatively, suitable capsules can be purchased from Appleton Papers Inc. of Appleton, Wisconsin USA.

In a preferred aspect the composition may comprise a deposition aid, preferably in addition to encapsulates. Preferred deposition aids are selected from the group consisting of  
10 cationic and nonionic polymers. Suitable polymers include cationic starches, cationic hydroxyethylcellulose, polyvinylformaldehyde, locust bean gum, mannans, xyloglucans, tamarind gum, polyethyleneterephthalate and polymers containing dimethylaminoethyl methacrylate, optionally with one or more monomers selected from the group comprising acrylic acid and acrylamide.

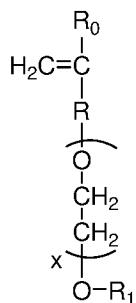
15 **Perfume.** Preferred compositions of the invention comprise perfume. Typically the composition comprises a perfume that comprises one or more perfume raw materials, selected from the group as described in WO08/87497. However, any perfume useful in a detergent may be used. A preferred method of incorporating perfume into the compositions of the invention is via an encapsulated perfume particle comprising either a water-soluble hydroxylic compound or  
20 melamine-formaldehyde or modified polyvinyl alcohol. In one aspect the encapsulate comprises (a) an at least partially water-soluble solid matrix comprising one or more water-soluble hydroxylic compounds, preferably starch; and (b) a perfume oil encapsulated by the solid matrix. In a further aspect the perfume may be pre-complexed with a polyamine, preferably a polyethylenimine so as to form a Schiff base.

25 **Polymers.** The detergent composition may comprise one or more polymers in addition to the DTI which may be polymeric. Examples are optionally modified carboxymethylcellulose, poly (ethylene glycol), poly(vinyl alcohol), polycarboxylates such as polyacrylates, maleic/acrylic acid copolymers and lauryl methacrylate/acrylic acid co-polymers and carboxylate polymers.

30 Suitable carboxylate polymers include maleate/acrylate random copolymer or polyacrylate homopolymer. The carboxylate polymer may be a polyacrylate homopolymer having a molecular weight of from 4,000 Da to 9,000 Da, or from 6,000 Da to 9,000 Da. Other suitable carboxylate polymers are co-polymers of maleic acid and acrylic acid, and may have a molecular weight in the range of from 4,000 Da to 90,000 Da.

Other suitable carboxylate polymers are co-polymers comprising: (i) from 50 to less than 98 wt% structural units derived from one or more monomers comprising carboxyl groups; (ii) from 1 to less than 49 wt% structural units derived from one or more monomers comprising sulfonate moieties; and (iii) from 1 to 49 wt% structural units derived from one or more types of monomers selected from ether bond-containing monomers represented by formulas (I) and (II):

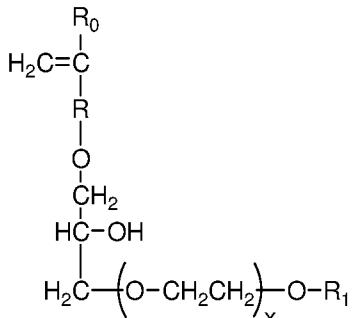
5 formula (I):



wherein in formula (I),  $\text{R}_0$  represents a hydrogen atom or  $\text{CH}_3$  group,  $\text{R}$  represents a  $\text{CH}_2$  group,

10  $\text{CH}_2\text{CH}_2$  group or single bond,  $\text{X}$  represents a number 0-5 provided  $\text{X}$  represents a number 1-5 when  $\text{R}$  is a single bond, and  $\text{R}_1$  is a hydrogen atom or C1 to C20 organic group;

formula (II)



15 in formula (II),  $\text{R}_0$  represents a hydrogen atom or  $\text{CH}_3$  group,  $\text{R}$  represents a  $\text{CH}_2$  group,  $\text{CH}_2\text{CH}_2$  group or single bond,  $\text{X}$  represents a number 0-5, and  $\text{R}_1$  is a hydrogen atom or C1 to C20 organic group.

The composition may comprise one or more amphiphilic cleaning polymers such as the compound having the following general structure: bis( $(\text{C}_2\text{H}_5\text{O})(\text{C}_2\text{H}_4\text{O})\text{n}$ ) $(\text{CH}_3)\text{-N}^+$  $\text{-C}_\text{x}\text{H}_{2\text{x}}\text{-N}^+$  $\text{-}(\text{CH}_3)$ -bis( $(\text{C}_2\text{H}_5\text{O})(\text{C}_2\text{H}_4\text{O})\text{n}$ ), wherein  $\text{n}$  = from 20 to 30, and  $\text{x}$  = from 3 to 8, or sulphated or sulphonated variants thereof. In one aspect, this polymer is sulphated or sulphonated to provide a zwitterionic soil suspension polymer.

The composition preferably comprises amphiphilic alkoxylated grease cleaning polymers which have balanced hydrophilic and properties such that they remove grease particles from fabrics and surfaces. Preferred amphiphilic alkoxylated grease cleaning polymers comprise a core structure and a plurality of alkoxyate groups attached to that core structure. These may 5 comprise alkoxylated polyalkylenimines, preferably having an inner polyethylene oxide block and an outer polypropylene oxide block. Typically these may be incorporated into the compositions of the invention in amounts of from 0.005 to 10 wt%, generally from 0.5 to 8 wt%.

Alkoxylated polycarboxylates such as those prepared from polyacrylates are useful herein to provide additional grease removal performance. Such materials are described in WO 10 91/08281 and PCT 90/01815. Chemically, these materials comprise polyacrylates having one ethoxy side-chain per every 7-8 acrylate units. The side-chains are of the formula  $-(\text{CH}_2\text{CH}_2\text{O})_m(\text{CH}_2)_n\text{CH}_3$  wherein m is 2-3 and n is 6-12. The side-chains are ester-linked to the polyacrylate "backbone" to provide a "comb" polymer type structure. The molecular weight can vary, but is typically in the range of about 2000 to about 50,000. Such alkoxylated polycarboxylates can 15 comprise from about 0.05% to about 10%, by weight, of the compositions herein.

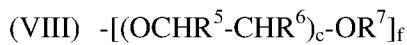
The composition may comprise polyethylene glycol polymers and these may be particularly preferred in compositions comprising mixed surfactant systems. Suitable polyethylene glycol polymers include random graft co-polymers comprising: (i) hydrophilic backbone comprising polyethylene glycol; and (ii) side chain(s) selected from the group 20 consisting of: C4-C25 alkyl group, polypropylene, polybutylene, vinyl ester of a saturated C1-C6 mono-carboxylic acid, C1-C 6 alkyl ester of acrylic or methacrylic acid, and mixtures thereof. Suitable polyethylene glycol polymers have a polyethylene glycol backbone with random grafted polyvinyl acetate side chains. The average molecular weight of the polyethylene glycol backbone can be in the range of from 2,000 Da to 20,000 Da, or from 4,000 Da to 8,000 Da. The molecular 25 weight ratio of the polyethylene glycol backbone to the polyvinyl acetate side chains can be in the range of from 1:1 to 1:5, or from 1:1.2 to 1:2. The average number of graft sites per ethylene oxide units can be less than 1, or less than 0.8, the average number of graft sites per ethylene oxide units can be in the range of from 0.5 to 0.9, or the average number of graft sites per ethylene oxide units can be in the range of from 0.1 to 0.5, or from 0.2 to 0.4. A suitable 30 polyethylene glycol polymer is Sokalan HP22.

Typically these are incorporated into the compositions of the invention in amounts from 0.005 to 10 wt%, more usually from 0.05 to 8 wt%.

Preferably the composition comprises one or more carboxylate polymer, such as a maleate/acrylate random copolymer or polyacrylate homopolymer. In one aspect, the

carboxylate polymer is a polyacrylate homopolymer having a molecular weight of from 4,000 Da to 9,000 Da, or from 6,000 Da to 9,000 Da. Typically these are incorporated into the compositions of the invention in amounts from 0.005 to 10 wt%, or from 0.05 to 8 wt%.

Preferably the composition comprises one or more soil release polymers. Examples 5 include soil release polymers having a structure as defined by one of the following Formulae (VI), (VII) or (VIII):



wherein:

15 a, b and c are from 1 to 200;

d, e and f are from 1 to 50;

Ar is a 1,4-substituted phenylene;

sAr is 1,3-substituted phenylene substituted in position 5 with  $SO_3Me$ ;

Me is Li, K, Mg/2, Ca/2, Al/3, ammonium, mono-, di-, tri-, or tetraalkylammonium

20 wherein the alkyl groups are  $C_1-C_{18}$  alkyl or  $C_2-C_{10}$  hydroxyalkyl, or mixtures thereof;

$R^1, R^2, R^3, R^4, R^5$  and  $R^6$  are independently selected from H or  $C_1-C_{18}$  n- or iso-alkyl; and

$R^7$  is a linear or branched  $C_1-C_{18}$  alkyl, or a linear or branched  $C_2-C_{30}$  alkenyl, or a cycloalkyl group with 5 to 9 carbon atoms, or a  $C_8-C_{30}$  aryl group, or a  $C_6-C_{30}$  arylalkyl group.

25 Suitable soil release polymers are polyester soil release polymers such as Repel-o-tex polymers, including Repel-o-tex SF, SF-2 and SRP6 supplied by Rhodia. Other suitable soil release polymers include Texcare polymers, including Texcare SRA100, SRA300, SRN100, SRN170, SRN240, SRN300 and SRN325 supplied by Clariant. Other suitable soil release polymers are Marloquest polymers, such as Marloquest SL supplied by Sasol.

30 Preferably the composition comprises one or more cellulosic polymer, including those selected from alkyl cellulose, alkyl alkoxyalkyl cellulose, carboxyalkyl cellulose, alkyl carboxyalkyl cellulose. Preferred cellulosic polymers are selected from the group comprising carboxymethyl cellulose, methyl cellulose, methyl hydroxyethyl cellulose, methyl carboxymethyl cellulose, and mixtures thereof. In one aspect, the carboxymethyl cellulose has a

degree of carboxymethyl substitution from 0.5 to 0.9 and a molecular weight from 100,000 Da to 300,000 Da.

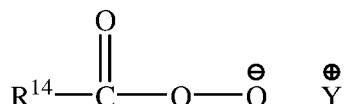
**Bleaching Agents.** It may be preferred for the composition to comprise one or more bleaching agents. Suitable bleaching agents other than bleaching catalysts include

5 photobleaches, bleach activators, hydrogen peroxide, sources of hydrogen peroxide, pre-formed peracids and mixtures thereof. In general, when a bleaching agent is used, the compositions of the present invention may comprise from about 0.1% to about 50% or even from about 0.1% to about 25% bleaching agent or mixtures of bleaching agents by weight of the subject composition. Examples of suitable bleaching agents include:

10 (1) photobleaches for example sulfonated zinc phthalocyanine sulfonated aluminium phthalocyanines, xanthene dyes and mixtures thereof;

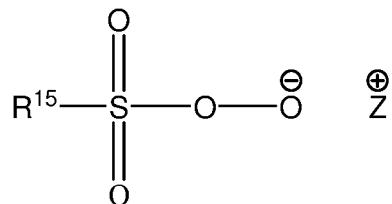
(2) pre-formed peracids: Suitable preformed peracids include, but are not limited to compounds selected from the group consisting of pre-formed peroxyacids or salts thereof typically a percarboxylic acids and salts, percarbonic acids and salts, perimidic acids and salts,

15 (3) peroxyomonosulfuric acids and salts, for example, Oxone ®, and mixtures thereof. Suitable examples include peroxycarboxylic acids or salts thereof, or peroxy sulphonnic acids or salts thereof. Typical peroxycarboxylic acid salts suitable for use herein have a chemical structure corresponding to the following chemical formula:



wherein:  $\text{R}^{14}$  is selected from alkyl, aralkyl, cycloalkyl, aryl or heterocyclic groups; the  $\text{R}^{14}$  group can be linear or branched, substituted or unsubstituted; having, when the peracid is, from 6 to 14 carbon atoms, or from 8 to 12 carbon atoms and, when the peracid is hydrophilic, less than 6 carbon atoms or even less than 4 carbon atoms and  $\text{Y}$  is any suitable counter-ion that achieves electric charge neutrality, preferably  $\text{Y}$  is selected from hydrogen, sodium or potassium. Preferably,  $\text{R}^{14}$  is a linear or branched, substituted or unsubstituted  $\text{C}_{6-9}$  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. Particularly preferred peroxyacids are phthalimido-peroxy-alkanoic acids, in particular  $\epsilon$ -phthalimido peroxy hexanoic acid (PAP). 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 peroxy sulphonic acid or salt thereof, typically having a chemical structure corresponding to the following chemical formula:



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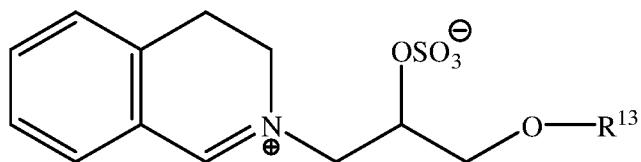
wherein:  $\text{R}^{15}$  is selected from alkyl, aralkyl, cycloalkyl, aryl or heterocyclic groups; the  $\text{R}^{15}$  group can be linear or branched, substituted or unsubstituted; and  $\text{Z}$  is any suitable counter-ion that achieves electric charge neutrality, preferably  $\text{Z}$  is selected from hydrogen, sodium or potassium. Preferably  $\text{R}^{15}$  is a linear or branched, substituted or unsubstituted C<sub>4-14</sub>, preferably C<sub>6-14</sub> alkyl. Preferably such bleach components may be present in the compositions of the invention in an amount from 0.01 to 50%, most preferably from 0.1% to 20%.

(3) sources of hydrogen peroxide, for example, inorganic perhydrate salts, including alkali metal salts such as sodium salts of perborate (usually mono- or tetra-hydrate), percarbonate, persulphate, perphosphate, persilicate salts and mixtures thereof. In one aspect of the invention the inorganic perhydrate salts are selected from the group consisting of sodium salts of perborate, percarbonate and mixtures thereof. When employed, inorganic perhydrate salts are typically present in amounts of from 0.05 to 40 wt%, or 1 to 30 wt% of the overall fabric and home care product and are typically incorporated into such fabric and home care products as a crystalline solid that may be coated. Suitable coatings include, inorganic salts such as alkali metal silicate, carbonate or borate salts or mixtures thereof, or organic materials such as water-soluble or dispersible polymers, waxes, oils or fatty soaps; and

(4) bleach activators having  $\text{R}-(\text{C}=\text{O})-\text{L}$  wherein  $\text{R}$  is an alkyl group, optionally branched, having, when the bleach activator is, from 6 to 14 carbon atoms, or from 8 to 12 carbon atoms and, when the bleach activator is hydrophilic, less than 6 carbon atoms or even less than 4 carbon atoms; and  $\text{L}$  is leaving group. Examples of suitable leaving groups are benzoic acid and derivatives thereof - especially benzene sulphonate. Suitable bleach activators include dodecanoyl oxybenzene sulphonate, decanoyl oxybenzene sulphonate, decanoyl oxybenzoic acid or salts thereof, 3,5,5-trimethyl hexanoyloxybenzene sulphonate, tetraacetyl ethylene diamine (TAED) and nonanoyloxybenzene sulphonate (NOBS). Suitable bleach activators are also disclosed in WO 98/17767. While any suitable bleach activator may be employed, in one aspect of the invention the subject composition may comprise NOBS, TAED or mixtures thereof.

(5) Bleach Catalysts. The compositions of the present invention may also include one or more bleach catalysts capable of accepting an oxygen atom from a peroxyacid and/or salt thereof, and transferring the oxygen atom to an oxidizable substrate. Suitable bleach catalysts include, but are not limited to: iminium cations and polyions; iminium zwitterions; modified amines; modified amine oxides; N-sulphonyl imines; N-phosphonyl imines; N-acyl imines; thiadiazole dioxides; perfluoroimines; cyclic sugar ketones and alpha amino-ketones and mixtures thereof. Suitable alpha amino ketones are for example as described in WO 2012/000846 A1, WO 2008/015443 A1, and WO 2008/014965 A1. Suitable mixtures are as described in USPA 2007/0173430 A1.

10 In one aspect, the bleach catalyst has a structure corresponding to general formula below:



15 wherein R<sup>13</sup> is selected from the group consisting of 2-ethylhexyl, 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;

(6) The composition may preferably comprise catalytic metal complexes. One preferred type of metal-containing bleach catalyst is a catalyst system 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 aluminum cations, and a sequestrate having defined stability constants for the catalytic and auxiliary metal cations, particularly ethylenediaminetetraacetic acid, ethylenediaminetetra(methylenephosphonic acid) and water-soluble salts thereof. Such catalysts are disclosed in U.S. 4,430,243.

25 If desired, the compositions herein can be catalyzed by means of a manganese compound. Such compounds and levels of use are well known in the art and include, for example, the manganese-based catalysts disclosed in U.S. 5,576,282.

20 Cobalt bleach catalysts useful herein are known, and are described, for example, in U.S. 5,597,936; U.S. 5,595,967. Such cobalt catalysts are readily prepared by known procedures, 30 such as taught for example in U.S. 5,597,936, and U.S. 5,595,967.

Compositions herein may also suitably include a transition metal complex of ligands such as bispidones (WO 05/042532 A1) and/or macropolycyclic rigid ligands - abbreviated as "MRLs". As a practical matter, and not by way of limitation, the compositions and processes herein can be adjusted to provide on the order of at least one part per hundred million of the active MRL species in the aqueous washing medium, and will typically provide from about 0.005 ppm to about 25 ppm, from about 0.05 ppm to about 10 ppm, or even from about 0.1 ppm to about 5 ppm, of the MRL in the wash liquor.

Suitable transition-metals in the instant transition-metal bleach catalyst include, for example, manganese, iron and chromium. Suitable MRLs include 5,12-diethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane.

Suitable transition metal MRLs are readily prepared by known procedures, such as taught for example in WO 00/32601, and U.S. 6,225,464.

When present, the source of hydrogen peroxide/peracid and/or bleach activator is generally present in the composition in an amount of from about 0.1 to about 60 wt%, from about 0.5 to about 40 wt % or even from about 0.6 to about 10 wt% based on the fabric and home care product. One or more peracids or precursors thereof may be used in combination with one or more hydrophilic peracid or precursor thereof.

Typically hydrogen peroxide source and bleach activator will be incorporated together. The amounts of hydrogen peroxide source and peracid or bleach activator may be selected such that the molar ratio of available oxygen (from the peroxide source) to peracid is from 1:1 to 35:1, or even 2:1 to 10:1.

**Surfactant.** Preferably the composition comprises a surfactant or surfactant system. The surfactant can be selected from nonionic, anionic, cationic, amphoteric, ampholytic, amphiphilic, zwitterionic, semi-polar nonionic surfactants and mixtures thereof. Preferred compositions comprise a mixture of surfactants/surfactant system. Preferred surfactant systems comprise one or more anionic surfactants, most preferably in combination with a co-surfactant, most preferably a nonionic and/or amphoteric and/or zwitterionic surfactant. Preferred surfactant systems comprise both anionic and nonionic surfactant, preferably in weight ratios from 90:1 to 2:3 or even 1:90. In some instances a weight ratio of anionic to nonionic surfactant of at least 1:1 is preferred. However a ratio below 10:1 may be preferred. When present, the total surfactant level is preferably from 0.1% to 60%, from 1% to 50% or even from 5% to 40% by weight of the subject composition.

Preferably the composition comprises an anionic detergents surfactant, preferably sulphate and/or sulphonate surfactants. Preferred examples include alkyl benzene sulphonates, alkyl

sulphates and alkyl alkoxylated sulphates. Preferred sulphonates are C<sub>10-13</sub> alkyl benzene sulphonate. Suitable alkyl benzene sulphonate (LAS) may be obtained, by sulphonating commercially available linear alkyl benzene (LAB); suitable LAB includes low 2-phenyl LAB, such as those supplied by Sasol under the tradename Isochem® or those supplied by Petresa under the tradename Petrelab®, other suitable LAB include high 2-phenyl LAB, such as those supplied by Sasol under the tradename Hyblene®. A suitable anionic detergents surfactant is alkyl benzene sulphonate that is obtained by DETAL catalyzed process, although other synthesis routes, such as HF, may also be suitable. In one aspect a magnesium salt of LAS is used.

Preferred sulphate detergents surfactants include alkyl sulphate, typically C<sub>8-18</sub> alkyl sulphate, or predominantly C<sub>12</sub> alkyl sulphate. A further preferred alkyl sulphate is alkyl alkoxylated sulphate, preferably a C<sub>8-18</sub> alkyl alkoxylated sulphate. Preferably the alkoxylation group is an ethoxylating group. Typically the alkyl alkoxylated sulphate has an average degree of alkoxylation of from 0.5 to 30 or 20, or from 0.5 to 10. Particularly preferred are C<sub>8-18</sub> alkyl ethoxylated sulphate having an average degree of ethoxylation of from 0.5 to 10, from 0.5 to 7, from 0.5 to 5 or even from 0.5 to 3.

The alkyl sulphate, alkyl alkoxylated sulphate and alkyl benzene sulphonates may be linear or branched, substituted or un-substituted. When the surfactant is branched, preferably the surfactant will comprise a mid-chain branched sulphate or sulphonate surfactant. Preferably the branching groups comprise C<sub>1-4</sub> alkyl groups, typically methyl and/or ethyl groups.

Preferably the composition comprises a nonionic detergents surfactant. Suitable non-ionic surfactants are selected from the group consisting of: C<sub>8</sub>-C<sub>18</sub> alkyl ethoxylates, such as, NEODOL® non-ionic surfactants from Shell; C<sub>6</sub>-C<sub>12</sub> alkyl phenol alkoxylates wherein the alkoxylate units may be ethyleneoxy units, propyleneoxy units or a mixture thereof; C<sub>12</sub>-C<sub>18</sub> alcohol and C<sub>6</sub>-C<sub>12</sub> alkyl phenol condensates with ethylene oxide/propylene oxide block polymers such as Pluronic® from BASF; C<sub>14</sub>-C<sub>22</sub> mid-chain branched alcohols; C<sub>14</sub>-C<sub>22</sub> mid-chain branched alkyl alkoxylates, typically having an average degree of alkoxylation of from 1 to 30; alkylpolysaccharides, in one aspect, alkylpolyglycosides; polyhydroxy fatty acid amides; ether capped poly(oxyalkylated) alcohol surfactants; and mixtures thereof.

Suitable non-ionic detergents surfactants include alkyl polyglucoside and/or an alkyl alkoxylated alcohol.

In one aspect, non-ionic detergents surfactants include alkyl alkoxylated alcohols, in one aspect C<sub>8-18</sub> alkyl alkoxylated alcohol, for example a C<sub>8-18</sub> alkyl ethoxylated alcohol, the alkyl alkoxylated alcohol may have an average degree of alkoxylation of from 1 to 80, preferably from 1 to 50, most preferably from 1 to 30, from 1 to 20, or from 1 to 10. In one aspect, the alkyl

alkoxylated alcohol may be a C<sub>8-18</sub> alkyl ethoxylated alcohol having an average degree of ethoxylation of from 1 to 10, from 1 to 7, more from 1 to 5 or from 3 to 7, or even below 3 or 2. The alkyl alkoxylated alcohol can be linear or branched, and substituted or un-substituted.

Suitable nonionic surfactants include those with the tradename Lutensol® ( BASF).

5 Suitable cationic detergents surfactants include alkyl pyridinium compounds, alkyl quaternary ammonium compounds, alkyl quaternary phosphonium compounds, alkyl ternary sulphonium compounds, and mixtures thereof.

Suitable cationic detergents surfactants are quaternary ammonium compounds having the general formula:

10 (R)(R<sub>1</sub>)(R<sub>2</sub>)(R<sub>3</sub>)N<sup>+</sup> X<sup>-</sup>

wherein, R is a linear or branched, substituted or unsubstituted C<sub>6-18</sub> alkyl or alkenyl moiety, R<sub>1</sub> and R<sub>2</sub> are independently selected from methyl or ethyl moieties, R<sub>3</sub> is a hydroxyl, hydroxymethyl or a hydroxyethyl moiety, X is an anion which provides charge neutrality, suitable anions include: halides, for example chloride; sulphate; and sulphonate. Suitable 15 cationic detergents surfactants are mono-C<sub>6-18</sub> alkyl mono-hydroxyethyl di-methyl quaternary ammonium chlorides. Highly suitable cationic detergents surfactants are mono-C<sub>8-10</sub> alkyl mono-hydroxyethyl di-methyl quaternary ammonium chloride, mono-C<sub>10-12</sub> alkyl mono-hydroxyethyl di-methyl quaternary ammonium chloride and mono-C<sub>10</sub> alkyl mono-hydroxyethyl di-methyl quaternary ammonium chloride.

20 Suitable amphoteric/zwitterionic surfactants include amine oxides and betaines.

Amine-neutralized anionic surfactants - Anionic surfactants of the present invention and adjunct anionic cosurfactants, may exist in an acid form, and said acid form may be neutralized to form a surfactant salt which is desirable for use in the present detergent compositions. Typical agents for neutralization include the metal counterion base such as hydroxides, eg, NaOH or 25 KOH. Further preferred agents for neutralizing anionic surfactants of the present invention and adjunct anionic surfactants or cosurfactants in their acid forms include ammonia, amines, or alkanolamines. Alkanolamines are preferred. Suitable non-limiting examples including monoethanolamine, diethanolamine, triethanolamine, and other linear or branched alkanolamines known in the art; for example, highly preferred alkanolamines include 2-amino-1-propanol, 1-30 aminopropanol, monoisopropanolamine, or 1-amino-3-propanol. Amine neutralization may be done to a full or partial extent, e.g. part of the anionic surfactant mix may be neutralized with sodium or potassium and part of the anionic surfactant mix may be neutralized with amines or alkanolamines.

**Builders.** Preferably the composition comprises one or more builders or a builder system. When a builder is used, the composition of the invention will typically comprise at least 1%, or at least 2% to 60% builder. Suitable builders include for example zeolite, phosphate, citrate, etc. It may be preferred that the composition comprises low levels of phosphate salt and/or zeolite, for example from 1 to 10 or 5 wt%. The composition may even be substantially free of strong builder; substantially free of strong builder means “no deliberately added” zeolite and/or phosphate. Typical zeolite builders include zeolite A, zeolite P and zeolite MAP. A typical phosphate builder is sodium tri-polyphosphate.

**Chelating Agent.** Preferably the composition comprises chelating agents and/or crystal growth inhibitor. Suitable molecules include copper, iron and/or manganese chelating agents and mixtures thereof. Suitable molecules include aminocarboxylates, aminophosphonates, succinates, salts thereof, and mixtures thereof. Non-limiting examples of suitable chelants for use herein include ethylenediaminetetracetates, N- (hydroxyethyl)ethylenediaminetriacetates, nitrilotriacetates, ethylenediamine tetrapropionate, triethylenetetraaminehexacetates, diethylenetriamine-pentaacetates, ethanoldiglycines, ethylenediaminetetrakis (methylenephosphonates), diethylenetriamine penta(methylene phosphonic acid) (DTPMP), ethylenediamine disuccinate (EDDS), hydroxyethanedimethyleneephosphonic acid (HEDP), methylglycinediacetic acid (MGDA), diethylenetriaminepentaacetic acid (DTPA), salts thereof, and mixtures thereof. Other nonlimiting examples of chelants of use in the present invention are found in U.S. Patent Nos. 7445644, 7585376 and 2009/0176684A1. Other suitable chelating agents for use herein are the commercial DEQUEST series, and chelants from Monsanto, DuPont, and Nalco, Inc.

**pH Modifiers.** pH modifiers may be incorporated to generate the desired pH. Any alkali or acid may be added known to those skilled in the art of detergent manufacture, for example, sodium or potassium hydroxide carbonate or silicate, citric acid, or stronger acids such as hydrochloric acid. Those pH modifiers which add buffering capacity may be particularly preferred.

**Silicate Salts.** The composition may preferably also contain silicate salts, such as sodium or potassium silicate. The composition may comprise from 0wt% to less than 10wt% silicate salt, to 9wt%, or to 8wt%, or to 7wt%, or to 6wt%, or to 5wt%, or to 4wt%, or to 3wt%, or even to 2wt%, and preferably from above 0wt%, or from 0.5wt%, or even from 1wt% silicate salt. A suitable silicate salt is sodium silicate.

**Dispersants.** The composition may preferably also contain dispersants. Suitable water-soluble organic materials include the homo- or co-polymeric acids or their salts, in which the

polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms.

**Enzyme Stabilisers.** The composition may preferably comprise enzyme stabilizers. Any conventional enzyme stabilizer may be used, for example by the presence of water-soluble sources of calcium and/or magnesium ions in the finished fabric and home care products that provide such ions to the enzymes. In case of aqueous compositions comprising protease, a reversible protease inhibitor, such as a boron compound including borate, or preferably 4-formyl phenylboronic acid, phenylboronic acid and derivatives thereof, or compounds such as calcium formate, sodium formate and 1,2-propane diol, diethylene glycol can be added to further improve stability.

#### **Fabric Shading Dye**

The composition may comprise fabric shading dye. Suitable fabric shading dye (sometimes referred to as hueing, bluing or whitening agents) typically provides a blue or violet shade to fabric. Fabric shading dyes can be used either alone or in combination to create a specific shade of hueing and/or to shade different fabric types. This may be provided for example by mixing a red and green-blue dye to yield a blue or violet shade. The fabric shading dye may be selected from any known chemical class of dye, including but not limited to acridine, anthraquinone (including polycyclic quinones), azine, azo (e.g., monoazo, disazo, trisazo, tetrakisazo, polyazo), including premetallized azo, benzodifurane and benzodifuranone, carotenoid, coumarin, cyanine, diazahemicyanine, diphenylmethane, formazan, hemicyanine, indigoids, methane, naphthalimides, naphthoquinone, nitro and nitroso, oxazine, phthalocyanine, pyrazoles, stilbene, styryl, triarylmethane, triphenylmethane, xanthenes and mixtures thereof.

Suitable fabric shading dyes include dyes and dye-clay conjugates. Preferred fabric shading dyes are selected from small molecule dyes and polymeric dyes. Suitable small molecule dyes include small molecule dyes selected from the group consisting of dyes falling into the Colour Index (C.I.) classifications of Acid, Direct, Basic, Reactive, Solvent or Disperse dyes for example that are classified as Blue, Violet, Red, Green or Black, and provide the desired shade either alone or in combination with other dyes or in combination with other adjunct ingredients. Dyes described as hydrolysed Reactive dyes, as described in EP-A-1794274 may also be included. In another aspect, suitable small molecule dyes include small molecule dyes selected from the group consisting of Colour Index (Society of Dyers and Colourists, Bradford, UK) numbers Direct Violet dyes such as 5, 7, 9, 11, 31, 35, 48, 51, 66, and 99, Direct Blue dyes such as 1, 71, 80 and 279, Acid Red dyes such as 17, 73, 52, 88 and 150, Acid Violet dyes such as 15, 17, 24, 43, 49 and 50, Acid Blue dyes such as 15, 17, 25, 29, 40, 45, 48, 75, 80, 83, 90 and

113, Acid Black dyes such as 1, Basic Violet dyes such as 1, 3, 4, 10 and 35, Basic Blue dyes such as 3, 16, 22, 47, 66, 75 and 159, Disperse or Solvent dyes such as those described in US 2008/034511 A1 or US 8,268,016 B2, or dyes as disclosed in US 7,208,459 B2, such as solvent violet 13 and mixtures thereof. In another aspect, suitable small molecule dyes include small molecule dyes selected from the group consisting of C. I. numbers Acid Violet 17, Acid Blue 80, Acid Violet 50, Direct Blue 71, Direct Violet 51, Direct Blue 1, Acid Red 88, Acid Red 150, Acid Blue 29, Acid Blue 113 or mixtures thereof.

5 Suitable polymeric dyes include polymeric dyes selected from the group consisting of polymers containing covalently bound (sometimes referred to as conjugated) chromogens, (dye-polymer conjugates), for example polymers with chromogens co-polymerized into the backbone of the polymer and mixtures thereof. Polymeric dyes include those described in WO2011/98355, US 2012/225803 A1, US 2012/090102 A1, WO2012/166768, US 7,686,892 B2, and WO2010/142503.

10 Other suitable polymeric dyes include polymeric dyes selected from the group consisting of fabric-substantive colorants sold under the name of Liquitint® (Milliken, Spartanburg, South Carolina, USA), dye-polymer conjugates formed from at least one reactive dye and a polymer selected from the group consisting of polymers comprising a moiety selected from the group consisting of a hydroxyl moiety, a primary amine moiety, a secondary amine moiety, a thiol moiety and mixtures thereof. In still another aspect, suitable polymeric dyes include polymeric 15 dyes selected from the group consisting of Liquitint® Violet CT, carboxymethyl cellulose (CMC) covalently bound to one or more reactive blue, reactive violet or reactive red dye such as CMC conjugated with C.I. Reactive Blue 19, sold by Megazyme, Wicklow, Ireland under the product name AZO-CM-CELLULOSE, product code S-ACMC, alkoxyLATED triphenyl-methane polymeric colourants, alkoxyLATED thiophene polymeric colourants, alkoxyLATED carbocyclic and 20 alkoxyLATED heterocyclic azo colourants, and mixtures thereof. Preferred polymeric dyes 25 comprise the optionally substituted alkoxyLATED dyes, such as alkoxyLATED triphenyl-methane polymeric colourants, alkoxyLATED thiophene polymeric colourants, alkoxyLATED carbocyclic and alkoxyLATED heterocyclic azo colourants, and mixtures thereof, such as the Liquitint dyes.

Preferred hueing dyes include the whitening agents found in WO 08/87497 A1, 30 WO2011/011799 and US 2012/129752 A1. Preferred hueing agents for use in the present invention may be the preferred dyes disclosed in these references, including those selected from Examples 1-42 in Table 5 of WO2011/011799. Other preferred dyes are disclosed in US 8,138,222. Other preferred dyes are disclosed in US 7,909,890 B2.

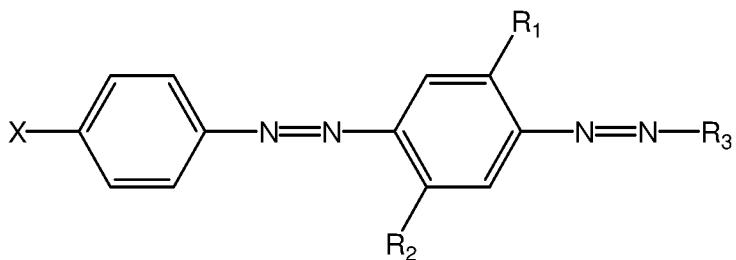
Suitable dye clay conjugates include dye clay conjugates selected from the group comprising at least one cationic/basic dye and a smectite clay, and mixtures thereof. In another aspect, suitable dye clay conjugates include dye clay conjugates selected from the group consisting of one cationic/basic dye and a clay selected from the group consisting of

5 Montmorillonite clay, Hectorite clay, Saponite clay and mixtures thereof. Examples of suitable cationic/basic dyes include C.I. Basic Yellow 1 through 108, C.I. Basic Orange 1 through 69, C.I. Basic Red 1 through 118, C.I. Basic Violet 1 through 51, C.I. Basic Blue 1 through 164, C.I. Basic Green 1 through 14, C.I. Basic Brown 1 through 23, CI Basic Black 1 through 11, In still another aspect, suitable dye clay conjugates include dye clay conjugates selected from the group 10 consisting of: Montmorillonite Basic Blue B7 C.I. 42595 conjugate, Montmorillonite Basic Blue B9 C.I. 52015 conjugate, Montmorillonite Basic Violet V3 C.I. 42555 conjugate, Montmorillonite Basic Green G1 C.I. 42040 conjugate, Montmorillonite Basic Red R1 C.I. 45160 conjugate, Montmorillonite C.I. Basic Black 2 conjugate, Hectorite Basic Blue B7 C.I. 42595 conjugate, Hectorite Basic Blue B9 C.I. 52015 conjugate, Hectorite Basic Violet V3 C.I. 42555 conjugate, Hectorite Basic Green G1 C.I. 42040 conjugate, Hectorite Basic Red R1 C.I. 45160 conjugate, Hectorite C.I. Basic Black 2 conjugate, Saponite Basic Blue B7 C.I. 42595 conjugate, Saponite Basic Blue B9 C.I. 52015 conjugate, Saponite Basic Violet V3 C.I. 42555 conjugate, Saponite Basic Green G1 C.I. 42040 conjugate, Saponite Basic Red R1 C.I. 45160 conjugate, Saponite C.I. Basic Black 2 conjugate and mixtures thereof.

20 The fabric shading dye or indeed other adjuncts made by organic synthesis routes such as pigment, optical brightener, polymer may be incorporated into the detergent composition as part of a reaction mixture which is the result of the organic synthesis for the adjunct with optional purification step(s). Such reaction mixtures generally comprise the adjunct itself and in addition may comprise un-reacted starting materials and/or by-products of the organic synthesis route.

25 Suitable polymeric fabric shading dyes are illustrated below. As with all such alkoxylated compounds, the organic synthesis may produce a mixture of molecules having different degrees of alkoxylation. Such mixtures may be used directly to provide the fabric shading dye, or may undergo a purification step.

The fabric shading dye may have the following structure:



wherein:

R<sub>1</sub> and R<sub>2</sub> are independently selected from the group consisting of: H; alkyl; alkoxy;

5 alkyleneoxy; alkyl capped alkyleneoxy; urea; and amido;

R<sub>3</sub> is a substituted aryl group;

X is a substituted group comprising sulfonamide moiety and optionally an alkyl and/or aryl moiety, and wherein the substituent group comprises at least one alkyleneoxy chain. The hueing dye may be a thiophene dye such as a thiophene azo dye, preferably alkoxyated. Optionally the dye may be substituted with at least one solubilising group selected from sulphonic, carboxylic or quaternary ammonium groups. Preferred dyes are Liquitint Dyes from Milliken Company.

10 10 Violet DD is particularly preferred.

The aforementioned fabric shading dyes can be used in combination (any mixture of fabric hueing agents can be used).

15 **Pigments.** Suitable pigments include pigments selected from the group consisting of flavanthrone, indanthrone, chlorinated indanthrone containing from 1 to 4 chlorine atoms, pyranthrone, dichloropyranthrone, monobromodichloropyranthrone, dibromodichloropyranthrone, tetrabromopyranthrone, perylene-3,4,9,10-tetracarboxylic acid diimide, wherein the imide groups may be unsubstituted or substituted by C1-C3 -alkyl or a phenyl or heterocyclic radical, and wherein the phenyl and heterocyclic radicals may additionally carry substituents which do not confer solubility in water, anthrapyrimidinecarboxylic acid amides, violanthrone, isoviolanthrone, dioxazine pigments, copper phthalocyanine which may contain up to 2 chlorine atoms per molecule, polychloro-copper phthalocyanine or polybromochloro-copper phthalocyanine containing up to 14 bromine atoms per molecule and mixtures thereof. Other suitable pigments are described in WO2008/090091. In another aspect, 20 suitable pigments include pigments selected from the group consisting of Ultramarine Blue (C.I. Pigment Blue 29), Ultramarine Violet (C.I. Pigment Violet 15), Monastral Blue and mixtures thereof. Particularly preferred are Pigment Blues 15 to 20, especially Pigment Blue 15 and/or 25 16. Other suitable pigments include those selected from the group consisting of Ultramarine Blue

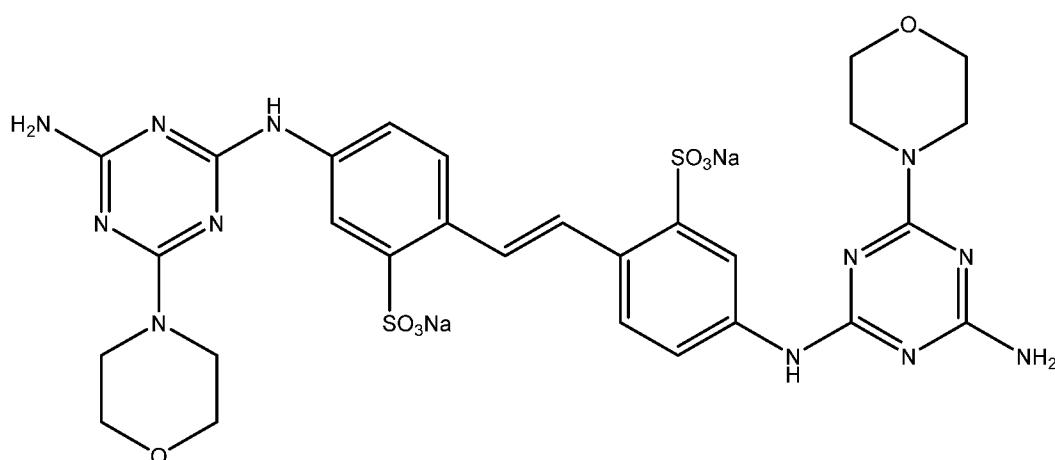
(C.I. Pigment Blue 29), Ultramarine Violet (C.I. Pigment Violet 15), Monastral Blue and mixtures thereof. Suitable hueing agents are described in more detail in US 7,208,459 B2.

The aforementioned fabric hueing agents can be used in mixtures of hueing agents and/or in mixtures with any pigment.

5 **Optical Brighteners.** Suitable examples of optical brighteners are for example stilbene brighteners, coumarinic brighteners, benzoxazole brighteners and mixtures thereof.

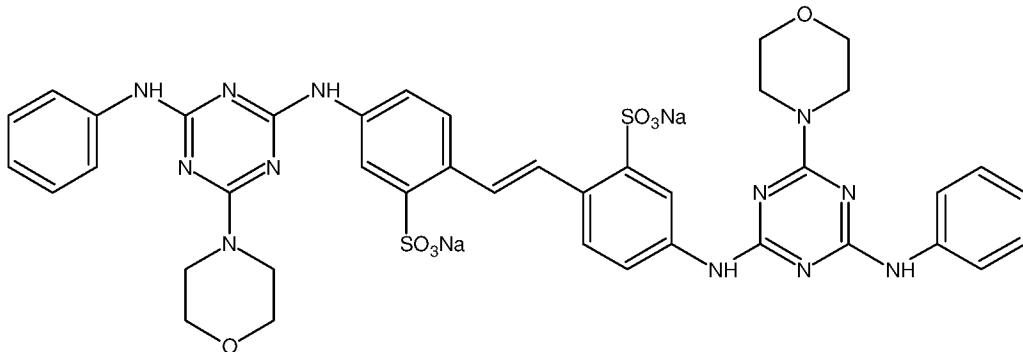
Diaminostilbene disulphonic acid type brighteners (hereinafter referred to as "DAS") are classified as hydrophilic in WO-A-98/52907. A commercial example of a DAS is Tinopal DMS (ex CIBA). Another type of low ClogP brightener is a distyrylbiphenyl brightener (hereinafter referred to as "DSBP"). A commercial example of this type of brightener is Tinopal CBS-X (also ex CIBA). Commercial optical brighteners which may be useful in the present invention can be classified into subgroups, which include, but are not limited to, derivatives of stilbene, pyrazoline, carboxylic acid, methinecyanines, dibenzothiophene-5,5-dioxide, azoles, 5- and 6-membered-ring heterocycles, and other miscellaneous agents. Particularly preferred brighteners 10 are selected from: sodium 2 (4-styryl-3-sulfophenyl) -2H-naphtho [1 , 2-d] triazole, disodium 4,4'-bis([4-anilino-6-(N-methyl-2-hydroxyethylamino)-1,3,5-triazin-2-yl]amino)stilbene-2,2'-disulfonate, disodium 4,4'-bis[(4-anilino-6-morpholino-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulfonate, and disodium 4,4'-bis(2-sulfostyryl)biphenyl. Other examples of such brighteners 15 are disclosed in "The Production and Application of Fluorescent Brightening Agents", M. Zahradnik, Published by John Wiley & Sons, New York (1982).

20 A preferred brightener has the structure below:



Suitable levels of brightener are from about 0.01, from about 0.05, from about 0.1 or even from about 0.2 wt % to upper levels of 0.5, of 0.75 or even 1.0 wt %.

25 A highly preferred optical brightener comprises C.I. fluorescent brightener 260 (preferably having the following structure:



A process for making C.I fluorescent brightener 260 is described in BE680847.

**Aesthetic Dyes.** The composition may comprise aesthetic dyes and/or pigments.

5 Suitable dyes include any conventional dye, typically small molecule or polymeric, used for colouring cleaning and/or treatment compositions. These are generally non-fabric shading dyes.

10 **Solvent System.** The present compositions may comprise a solvent system for example comprising water alone or mixtures of organic solvents either without or with water. Preferred organic solvents include 1,2-propanediol, ethanol, glycerol, dipropylene glycol, methyl propane diol and mixtures thereof. Other lower alcohols, C1-C4 alkanolamines such as 15 monoethanolamine and triethanolamine, can also be used. Solvent systems can be absent, for example from anhydrous solid embodiments of the invention, but more typically are present at levels in the range of from about 0.1% to about 98%, preferably at least about 1% to about 50%, more usually from about 5% to about 25%. Such solvent systems may be particularly useful for 20 pre-mixing with the brightener prior to mixing the brightener with other components in the detergent composition. Alternatively or in addition, surfactant(s) may be pre-mixed with the brightener. In such a preferred embodiment, the surfactant pre-mixed with the brightener comprises at least 25 wt% or at least 50 wt% (based on the total weight of the surfactant) of nonionic surfactant.

25 In some embodiments of the invention, the composition is in the form of a structured liquid. Such structured liquids can either be internally structured, whereby the structure is formed by primary ingredients (e.g. surfactant material) and/or externally structured by providing a three dimensional matrix structure using secondary ingredients (e.g. polymers, clay and/or silicate material), for use e.g. as thickeners. The composition may comprise a structurant, preferably from 0.01wt% to 5wt%, from 0.1wt% to 2.0wt% structurant. Examples of suitable structurants are given in US2006/0205631A1, US2005/0203213A1, US7294611, US6855680. The structurant is typically selected from the group consisting of diglycerides and triglycerides, ethylene glycol distearate, microcrystalline cellulose, cellulose-based materials, microfiber

cellulose, ally modified alkali-swellable emulsions such as Polygel W30 (3VSigma), biopolymers, xanthan gum, gellan gum, hydrogenated castor oil, derivatives of hydrogenated castor oil such as non-ethoxylated derivatieves thereof and mixtures thereof, in particular, those selected from the group of hydrogenated castor oil, derivatives of hydrogenated castor oil,

5 microfibullar cellulose, hydroxyfunctional crystalline materials, long chain fatty alcohols, 12-hydroxystearic acids, clays and mixtures thereof. A preferred structurant is described in . US Patent No. 6,855,680 which defines suitable hydroxyfunctional crystalline materials in detail. Preferred is hydrogenated castor oil. Non-limiting examples of useful structurants include.. Such structurants have a thread-like structuring system having a range of aspect ratios. Other 10 suitable structurants and the processes for making them are described in WO2010/034736.

The composition of the present invention may comprise a high melting point fatty compound. The high melting point fatty compound useful herein has a melting point of 25°C or higher, and is selected from the group consisting of fatty alcohols, fatty acids, fatty alcohol derivatives, fatty acid derivatives, and mixtures thereof. Such compounds of low melting point 15 are not intended to be included in this section. Non-limiting examples of the high melting point compounds are found in International Cosmetic Ingredient Dictionary, Fifth Edition, 1993, and CTFA Cosmetic Ingredient Handbook, Second Edition, 1992. When present, the high melting point fatty compound is preferably included in the composition at a level of from 0.1% to 40%, preferably from 1% to 30%, more preferably from 1.5% to 16% by weight of the composition, 20 from 1.5% to 8% in view of providing improved conditioning benefits such as slippery feel during the application to wet hair, softness and moisturized feel on dry hair.

**Cationic Polymer.** The compositions of the present invention may contain a cationic polymer. Concentrations of the cationic polymer in the composition typically range from 0.05% to 3%, in another embodiment from 0.075% to 2.0%, and in yet another embodiment from 0.1% 25 to 1.0%. Suitable cationic polymers will have cationic charge densities of at least 0.5 meq/gm, in another embodiment at least 0.9 meq/gm, in another embodiment at least 1.2 meq/gm, in yet another embodiment at least 1.5 meq/gm, but in one embodiment also less than 7 meq/gm, and in another embodiment less than 5 meq/gm, at the pH of intended use of the composition, which pH will generally range from pH 3 to pH 9, in one embodiment between pH 4 and pH 8. Herein, 30 "cationic charge density" of a polymer refers to the ratio of the number of positive charges on the polymer to the molecular weight of the polymer. The average molecular weight of such suitable cationic polymers will generally be between 10,000 and 10 million, in one embodiment between 50,000 and 5 million, and in another embodiment between 100,000 and 3 million.

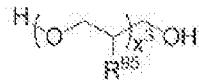
Suitable cationic polymers for use in the compositions of the present invention contain cationic nitrogen-containing moieties such as quaternary ammonium or cationic protonated amino moieties. Any anionic counterions can be used in association with the cationic polymers so long as the polymers remain soluble in water, in the composition, or in a coacervate phase of the composition, and so long as the counterions are physically and chemically compatible with the essential components of the composition or do not otherwise unduly impair product performance, stability or aesthetics. Nonlimiting examples of such counterions include halides (e.g., chloride, fluoride, bromide, iodide), sulfate and methylsulfate.

Nonlimiting examples of such polymers are described in the CTFA Cosmetic Ingredient Dictionary, 3rd edition, edited by Estrin, Crosley, and Haynes, (The Cosmetic, Toiletry, and Fragrance Association, Inc., Washington, D.C. (1982)).

Other suitable cationic polymers for use in the composition include polysaccharide polymers, cationic guar gum derivatives, quaternary nitrogen-containing cellulose ethers, synthetic polymers, copolymers of etherified cellulose, guar and starch. When used, the cationic polymers herein are either soluble in the composition or are soluble in a complex coacervate phase in the composition formed by the cationic polymer and the anionic, amphoteric and/or zwitterionic surfactant component described hereinbefore. Complex coacervates of the cationic polymer can also be formed with other charged materials in the composition.

Suitable cationic polymers are described in U.S. Pat. Nos. 3,962,418; 3,958,581; and U.S. Publication No. 2007/0207109A1.

**Nonionic Polymer.** The composition of the present invention may include a nonionic polymer as a conditioning agent. Polyalkylene glycols having a molecular weight of more than 1000 are useful herein. Useful are those having the following general formula:



wherein R95 is selected from the group consisting of H, methyl, and mixtures thereof. Conditioning agents, and in particular silicones, may be included in the composition. The conditioning agents useful in the compositions of the present invention typically comprise a water insoluble, water dispersible, non-volatile, liquid that forms emulsified, liquid particles. Suitable conditioning agents for use in the composition are those conditioning agents characterized generally as silicones (e.g., silicone oils, cationic silicones, silicone gums, high refractive silicones, and silicone resins), organic conditioning oils (e.g., hydrocarbon oils, polyolefins, and fatty esters) or combinations thereof, or those conditioning agents which otherwise form liquid, dispersed particles in the aqueous surfactant matrix herein. Such

conditioning agents should be physically and chemically compatible with the essential components of the composition, and should not otherwise unduly impair product stability, aesthetics or performance.

The concentration of the conditioning agent in the composition should be sufficient to 5 provide the desired conditioning benefits. Such concentration can vary with the conditioning agent, the conditioning performance desired, the average size of the conditioning agent particles, the type and concentration of other components, and other like factors.

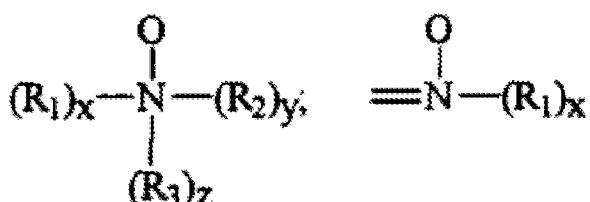
The concentration of the silicone conditioning agent typically ranges from about 0.01% to about 10%. Non-limiting examples of suitable silicone conditioning agents, and optional 10 suspending agents for the silicone, are described in U.S. Reissue Pat. No. 34,584, U.S. Pat. Nos. 5,104,646; 5,106,609; 4,152,416; 2,826,551; 3,964,500; 4,364,837; 6,607,717; 6,482,969; 5,807,956; 5,981,681; 6,207,782; 7,465,439; 7,041,767; 7,217,777; US Patent Application Nos. 2007/0286837A1; 2005/0048549A1; 2007/0041929A1; British Pat. No. 849,433; German Patent No. DE 10036533, which are all incorporated herein by reference; Chemistry and Technology of 15 Silicones, New York: Academic Press (1968); General Electric Silicone Rubber Product Data Sheets SE 30, SE 33, SE 54 and SE 76; Silicon Compounds, Petrarch Systems, Inc. (1984); and in Encyclopedia of Polymer Science and Engineering, vol. 15, 2d ed., pp 204-308, John Wiley & Sons, Inc. (1989).

**Dye Transfer Inhibitor (DTI).** The cleaning and/or treatment compositions preferably 20 comprise one or mixtures of more than one dye transfer inhibiting agents. Suitable dye transfer inhibitors are selected from the group consisting of: polyvinylpyrrolidone polymers, polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinyloxazolidones, polyvinylimidazoles and mixtures thereof. Other suitable DTIs are triazines as described in WO2012/095354, polymerized benzoxazines as described in 25 WO2010/130624, polyvinyl tetrazoles as described in DE 102009001144A, porous polyamide particles as described in WO2009/127587 and insoluble polymer particles as described in WO2009/124908. Other suitable DTIs are described in WO2012/004134, or polymers selected 30 from the group consisting of (a) amphiphilic alkoxylated polyamines, amphiphilic graft copolymers, zwitterionic soil suspension polymers, manganese phthalocyanines, peroxidases and mixtures thereof.

Preferred classes of DTI include but are not limited to polyvinylpyrrolidone polymers, polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinyloxazolidones, polyvinylimidazoles and mixtures thereof. More specifically, the polyamine N-oxide polymers preferred for use herein contain units having the following

structural formula: R-AX-P; wherein P is a polymerizable unit to which an N-O group can be attached or the N-O group can form part of the polymerizable unit or the N-O group can be attached to both units; A is one of the following structures: -NC(O)-, -C(O)O-, -S-, -O-, -N=; x is 0 or 1; and R is aliphatic, ethoxylated aliphatics, aromatics, heterocyclic or alicyclic groups or 5 any combination thereof to which the nitrogen of the N-O group can be attached or the N-O group is part of these groups. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyridine, pyrrole, imidazole, pyrrolidine, piperidine and derivatives thereof.

The N-O group can be represented by the following general structures:



10 wherein R1, R2, R3 are aliphatic, aromatic, heterocyclic or alicyclic groups or combinations thereof; x, y and z are 0 or 1; and the nitrogen of the N-O group can be attached or form part of any of the aforementioned groups. The amine oxide unit of the polyamine N-oxides has a pKa < 10, preferably pKa < 7, more preferred pKa < 6.

Any polymer backbone can be used as long as the amine oxide polymer formed is water-soluble and has dye transfer inhibiting properties. Examples of suitable polymeric backbones are 15 polyvinyls, polyalkylenes, polyesters, polyethers, polyamide, polyimides, polyacrylates and mixtures thereof. These polymers include random or block copolymers where one monomer type is an amine N-oxide and the other monomer type is an N-oxide. The amine N-oxide polymers typically have a ratio of amine to the amine N-oxide of 10:1 to 1:1,000,000. However, the 20 number of amine oxide groups present in the polyamine oxide polymer can be varied by appropriate copolymerization or by an appropriate degree of N-oxidation. The polyamine oxides can be obtained in almost any degree of polymerization.

Typically, the average molecular weight is within the range of 500 to 1,000,000; more preferred 1,000 to 500,000; most preferred 5,000 to 100,000. This preferred class of materials 25 can be referred to as "PVNO".

The most preferred polyamine N-oxide useful in the detergent compositions herein is poly(4-vinylpyridine-N-oxide) which as an average molecular weight of about 50,000 and an amine to amine N-oxide ratio of about 1:4.

Copolymers of N-vinylpyrrolidone and N-vinylimidazole polymers (referred to as a class 30 class "PVPVI") are also preferred for use herein. Preferably the PVPVI has an average molecular

weight range from 5,000 to 1,000,000, more preferably from 5,000 to 200,000, and most preferably from 10,000 to 20,000. (The average molecular weight range is determined by light scattering as described in Barth, et al.,

Chemical Analysis, Vol 113. "Modem Methods of Polymer Characterization", the disclosures of which are incorporated herein by reference.) The PVPVI copolymers typically have a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1:1 to 0.2:1, more preferably from 0.8:1 to 0.3:1, most preferably from 0.6:1 to 0.4:1.

These copolymers can be either linear or branched.

The present invention compositions also may employ a polyvinylpyrrolidone ("PVP") having an average molecular weight of from about 5,000 to about 400,000, preferably from about 5,000 to about 200,000, and more preferably from about 5,000 to about 50,000. PVP's are known to persons skilled in the detergent field; see, for example, EP-A-262,897 and EP-A-256,696, incorporated herein by reference.

Compositions containing PVP can also contain polyethylene glycol ("PEG") having an average molecular weight from about 500 to about 100,000, preferably from about 1,000 to about 10,000. Preferably, the ratio of PEG to PVP on a ppm basis delivered in wash solutions is from about 2:1 to about 50:1, and more preferably from about 3:1 to about 10:1.

A mixed polymer system comprising copolymers of (a) N-vinylpyrrolidone and N-vinylimidazole and (b) polyamine N-oxide polymers, particularly poly 4-vinylpyridine N-oxide are a particularly preferred DTI system, particularly preferred in weight ratios of (a):(b) of 5:1 to 1:5. Preferred molecular weights for the DTI essential to the present invention are from 1000 to 250000 Daltons, more preferably from 2000 to 150000 or even from 8000 to 100000 Daltons.

Suitable examples include PVP-K15, PVP-K30, ChromaBond S-400, ChromaBond S-403E and Chromabond S-100 from Ashland Aqualon, and Sokalan® HP165, Sokalan® HP50, Sokalan® HP53, Sokalan® HP59, Sokalan® HP 56K , Sokalan® HP 66 from BASF.

The inventors have found that the compositions comprising optical brightener and DTI provide significant increase in whiteness and this is surprising because typically DTIs reduce the efficacy of optical brighteners.

The dye transfer inhibiting agent may be present at levels from about 0.0001% to about 15%, from about 0.01% to about 10%, preferably from about 0.01% to about 5% by weight of the composition.

**Organic Conditioning Oil.** The compositions of the present invention may also comprise from about 0.05% to about 3% of at least one organic conditioning oil as the

conditioning agent, either alone or in combination with other conditioning agents, such as the silicones (described herein). Suitable conditioning oils include hydrocarbon oils, polyolefins, and fatty esters. Also suitable for use in the compositions herein are the conditioning agents described by the Procter & Gamble Company in U.S. Pat. Nos. 5,674,478, and 5,750,122. Also  
5 suitable for use herein are those conditioning agents described in U.S. Pat. Nos. 4,529,586, 4,507,280, 4,663,158, 4,197,865, 4,217, 914, 4,381,919, and 4,422, 853.

**Hygiene Agent.** The compositions of the present invention may also comprise components to deliver hygiene and/or malodour benefits such as one or more of zinc ricinoleate, thymol, quaternary ammonium salts such as Bardac®, polyethylenimines (such as Lupasol® from BASF) and zinc complexes thereof, silver and silver compounds, especially those designed to slowly release Ag+ or nano-silver dispersions.

**Probiotics.** The composition may comprise probiotics, such as those described in WO2009/043709.

**Suds Boosters.** The composition may preferably comprise suds boosters if high sudsing is desired. Suitable examples are the C10-C16 alkanolamides or C10-C14 alkyl sulphates, which are preferably incorporated at 1%-10% levels. The C10-C14 monoethanol and diethanol amides illustrate a typical class of such suds boosters. Use of such suds boosters with high sudsing adjunct surfactants such as the amine oxides, betaines and sultaines noted above is also advantageous. If desired, water-soluble magnesium and/or calcium salts such as MgCl2, MgSO4, CaCl2, CaSO4 and the like, can be added at levels of, typically, 0.1%-2%, to provide additional suds and to enhance grease removal performance.

**Suds Suppressor.** Compounds for reducing or suppressing the formation of suds may be incorporated into the compositions of the present invention. Suds suppression can be of particular importance in the so-called "high concentration cleaning process" as described in U.S. Pat. No. 4,489,455 and 4,489,574, and in front-loading -style washing machines. A wide variety of materials may be used as suds suppressors, and suds suppressors are well known to those skilled in the art. See, for example, Kirk Othmer Encyclopedia of Chemical Technology, Third Edition, Volume 7, pages 430-447 (John Wiley & Sons, Inc., 1979). Examples of suds suppressors include monocarboxylic fatty acid and soluble salts therein, high molecular weight hydrocarbons such as paraffin, fatty acid esters (e.g., fatty acid triglycerides), fatty acid esters of monovalent alcohols, aliphatic C18-C40 ketones (e.g., stearone), N-alkylated amino triazines, waxy hydrocarbons preferably having a melting point below about 100 °C, silicone suds suppressors, and secondary alcohols. Suds suppressors are described in U.S. Pat. No. 2,954,347; 4,265,779; 4,265,779; 3,455,839; 3,933,672; 4,652,392; 4,978,471; 4,983,316; 5,288,431;

4,639,489; 4,749,740; and 4,798,679; 4,075,118; European Patent Application No. 89307851.9; EP 150,872; and DOS 2,124,526.

For any detergent compositions to be used in automatic laundry washing machines, suds should not form to the extent that they overflow the washing machine. Suds suppressors, when utilized, are preferably present in a "suds suppressing amount. By "suds suppressing amount" is meant that the formulator of the composition can select an amount of this suds controlling agent that will sufficiently control the suds to result in a low-sudsing laundry detergent for use in automatic laundry washing machines. The compositions herein will generally comprise from 0% to 10% of suds suppressor. When utilized as suds suppressors, monocarboxylic fatty acids, and salts therein, will be present typically in amounts up to 5%, by weight, of the detergent composition. Preferably, from 0.5% to 3% of fatty monocarboxylate suds suppressor is utilized. Silicone suds suppressors are typically utilized in amounts up to 2.0%, by weight, of the detergent composition, although higher amounts may be used. Monostearyl phosphate suds suppressors are generally utilized in amounts ranging from 0.1% to 2%, by weight, of the composition. Hydrocarbon suds suppressors are typically utilized in amounts ranging from 0.01% to 5.0%, although higher levels can be used. The alcohol suds suppressors are typically used at 0.2%-3% by weight of the finished compositions.

**Pearlescent Agents.** Pearlescent agents as described in WO2011/163457 may be incorporated into the compositions of the invention.

**Perfume.** Preferably the composition comprises a perfume, preferably in the range from 0.001 to 3wt%, most preferably from 0.1 to 1 wt%. Many suitable examples of perfumes are provided in the CTFA (Cosmetic, Toiletry and Fragrance Association) 1992 International Buyers Guide, published by CFTA Publications and OPD 1993 Chemicals Buyers Directory 80<sup>th</sup> Annual Edition, published by Schnell Publishing Co. It is usual for a plurality of perfume components to be present in the compositions of the invention, for example four, five, six, seven or more. In perfume mixtures preferably 15 to 25 wt% are top notes. Top notes are defined by Poucher (Journal of the Society of Cosmetic Chemists 6(2):80 [1995]). Preferred top notes include rose oxide, citrus oils, linalyl acetate, lavender, linalool, dihydromyrcenol and cis-3-hexanol.

**Packaging.** Any conventional packaging may be used and the packaging may be fully or partially transparent so that the consumer can see the colour of the product which may be provided or contributed to by the colour of the dyes essential to the invention. UV absorbing compounds may be included in some or all of the packaging.

#### **Process of Making Compositions**

The compositions of the invention may be solid (for example granules or tablets) or liquid form. Preferably the compositions are in liquid form. They may be made by any process chosen by the formulator, non-limiting examples of which are described in the examples and in U.S. 4,990,280; U.S. 20030087791A1; U.S. 20030087790A1; U.S. 20050003983A1; U.S. 5 20040048764A1; U.S. 4,762,636; U.S. 6,291,412; U.S. 20050227891A1; EP 1070115A2; U.S. 5,879,584; U.S. 5,691,297; U.S. 5,574,005; U.S. 5,569,645; U.S. 5,565,422; U.S. 5,516,448; U.S. 5,489,392; U.S. 5,486.

When in the form of a liquid, the compositions of the invention may be aqueous (typically above 2 wt% or even above 5 or 10 wt% total water, up to 90 or up to 80wt% or 70 wt% total water) or non-aqueous (typically below 2 wt% total water content). Typically the compositions of the invention will be in the form of an aqueous solution or uniform dispersion or suspension of optical brightener, DTI and optional additional adjunct materials, some of which may normally be in solid form, that have been combined with the normally liquid components of the composition, such as the liquid alcohol ethoxylate nonionic, the aqueous liquid carrier, and any other normally liquid optional ingredients. Such a solution, dispersion or suspension will be acceptably phase stable. When in the form of a liquid, the detergents of the invention preferably have viscosity from 1 to 1500 centipoises (1-1500 mPa\*s), more preferably from 100 to 1000 centipoises (100-1000 mPa\*s), and most preferably from 200 to 500 centipoises (200-500 mPa\*s) at 20s-1 and 21°C. Viscosity can be determined by conventional methods. Viscosity may be 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 20s-1 and low shear viscosity at 0.05-1 can be obtained from a logarithmic shear rate sweep from 0.1-1 to 25-1 in 3 minutes time at 21C. The preferred rheology described therein may be achieved using internal existing structuring with detergent ingredients or by employing an external rheology modifier. More preferably the detergents, such as detergent liquid compositions have a high shear rate viscosity of from about 100 centipoise to 1500 centipoise, more preferably from 100 to 1000 cps. Unit Dose detergents, such as detergent liquid compositions have high shear rate viscosity of from 400 to 1000cps. Detergents such as laundry softening compositions typically have high shear rate viscosity of from 10 to 1000, more preferably from 10 to 800 cps, most preferably from 10 to 500 cps. Hand dishwashing compositions have high shear rate viscosity of from 300 to 4000 cps, more preferably 300 to 1000 cps.

The cleaning and/or treatment compositions in the form of a liquid herein can be prepared by combining the components thereof in any convenient order and by mixing, e.g., agitating, the resulting component combination to form a phase stable liquid detergent composition. In a

process for preparing such compositions, a liquid matrix is formed containing at least a major proportion, or even substantially all, of the liquid components, e.g., nonionic surfactant, the non-surface active liquid carriers and other optional liquid components, with the liquid components being thoroughly admixed by imparting shear agitation to this liquid combination. For example,

5 rapid stirring with a mechanical stirrer may usefully be employed. While shear agitation is maintained, substantially all of any anionic surfactants and the solid form ingredients can be added. Agitation of the mixture is continued, and if necessary, can be increased at this point to form a solution or a uniform dispersion of insoluble solid phase particulates within the liquid phase. After some or all of the solid-form materials have been added to this agitated mixture,

10 particles of any enzyme material to be included, e.g., enzyme prills, are incorporated. As a variation of the composition preparation procedure hereinbefore described, one or more of the solid components may be added to the agitated mixture as a solution or slurry of particles premixed with a minor portion of one or more of the liquid components. After addition of all of the composition components, agitation of the mixture is continued for a period of time sufficient

15 to form compositions having the requisite viscosity and phase stability characteristics.

Frequently this will involve agitation for a period of from about 30 to 60 minutes.

**Pouches.** In a preferred embodiment of the invention, the composition is provided in the form of a unitized dose, either tablet form or preferably in the form of a liquid/solid (optionally granules)/gel/paste held within a water-soluble film in what is known as a pouch or pod. The

20 composition can be encapsulated in a single or multi-compartment pouch. Multi-compartment pouches are described in more detail in EP-A-2133410. Shading or non-shading dyes or pigments or other aesthetics may also be used in one or more compartments.

Suitable film for forming the pouches is soluble or dispersible in water, and preferably has a water-solubility/dispersibility of at least 50%, preferably at least 75% or even at least 95%,

25 as measured by the method set out here after using a glass-filter with a maximum pore size of 20 microns:

50 grams  $\pm$  0.1 gram of pouch material 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 through a folded qualitative sintered-glass filter with a pore size as defined above (max. 20 micron). 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 dispersability can be calculated. Preferred film materials are polymeric materials. The film material can be obtained, for example, by casting, blow-moulding, extrusion or blown extrusion

of the polymeric material, as known in the art. Preferred polymers, copolymers or derivatives thereof suitable for use as pouch material are selected from polyvinyl alcohols, polyvinyl pyrrolidone, polyalkylene oxides, acrylamide, 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 xanthum and carragum. More preferred polymers are selected from polyacrylates and water-soluble acrylate copolymers, methylcellulose, carboxymethylcellulose sodium, dextrin, ethylcellulose, hydroxyethyl cellulose, hydroxypropyl methylcellulose, maltodextrin, polymethacrylates, and most preferably selected from polyvinyl alcohols, polyvinyl alcohol copolymers and hydroxypropyl methyl cellulose (HPMC), and combinations thereof. 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 about 1000 to 1,000,000, more preferably from about 10,000 to 300,000 yet more preferably from about 20,000 to 150,000. Mixtures of polymers can also be used as the pouch material. This can be beneficial to control the mechanical and/or dissolution properties of the compartments or pouch, depending on the application thereof and the required needs. Suitable mixtures include for example mixtures wherein one polymer has a higher water-solubility than another polymer, and/or one polymer has a higher mechanical strength than another polymer. Also suitable are mixtures of polymers having different weight average molecular weights, for example a mixture of PVA or a copolymer thereof of a weight average molecular weight of about 10,000- 40,000, preferably around 20,000, and of PVA or copolymer thereof, with a weight average molecular weight of about 100,000 to 300,000, preferably around 150,000. Also suitable herein are polymer blend compositions, for example comprising hydrolytically degradable and water-soluble polymer blends such as polylactide and polyvinyl alcohol, obtained by mixing polylactide and polyvinyl alcohol, typically comprising about 1-35% by weight polylactide and about 65% to 99% by weight polyvinyl alcohol. Preferred for use herein are polymers which are from about 60% to about 98% hydrolysed, preferably about 80% to about 90% hydrolysed, to improve the dissolution characteristics of the material.

Naturally, different film material and/or films of different thickness may be employed in making the compartments of the present invention. A benefit in selecting different films is that the resulting compartments may exhibit different solubility or release characteristics.

Most preferred film materials are PVA films known under the MonoSol trade reference M8630, M8900, H8779 (as described in the Applicants co-pending applications ref 44528 and

11599) and those described in US 6 166 117 and US 6 787 512 and PVA films of corresponding solubility and deformability characteristics.

The film material herein can also comprise one or more additive ingredients. For example, it can be beneficial to add plasticisers, for example glycerol, ethylene glycol, 5 diethyleneglycol, propylene glycol, sorbitol and mixtures thereof. Other additives include functional detergent additives to be delivered to the wash water, for example organic polymeric dispersants, etc.

Bittering agent may be incorporated into a pouch or pod, either by incorporation in the composition inside the pouch, and/or by coating onto the film.

10 **Method of Use.** An effective amount of such a composition is added to water to result in a concentration of the surfactant system no greater than 1g/l, for example in a conventional fabric automatic washing machine, to form such aqueous laundering solutions. The aqueous washing solution so formed is then contacted, typically under agitation, with the fabrics to be laundered/treated therewith.

15 The method of laundering fabric or textile may be carried out in a top-loading or front-loading automatic washing machine, or can be used in a hand-wash laundry application. In these applications, 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) is not included when determining the volume of the wash liquor.

20 The wash liquor may comprise 40 litres or less of water, or 30 litres or less, or 20 litres or less, or 10 litres or less, or 8 litres or less, or even 6 litres or less of water. The wash liquor may comprise from above 0 to 15 litres, or from 2 litres, and to 12 litres, or even to 8 litres of water. Typically from 0.01kg to 2kg of fabric per litre of wash liquor is dosed into said wash liquor.

25 Typically from 0.01kg, or from 0.05kg, or from 0.07kg, or from 0.10kg, or from 0.15kg, or from 0.20kg, or from 0.25kg fabric per litre of wash liquor is dosed into said wash liquor. Optionally, 50g or less, or 45g or less, or 40g or less, or 35g or less, or 30g or less, or 25g or less, or 20g or less, or even 15g or less, or even 10g or less of the composition is contacted to water to form the wash liquor. The water to fabric ratio is typically from about 1:1 to about 30:1. Typically the wash liquor comprising the detergent of the invention has a pH of from 3 to 11.5.

30 In one aspect, such method comprises the steps of optionally washing and/or rinsing said surface or fabric, contacting said surface or fabric with any composition disclosed in this specification then optionally washing and/or rinsing said surface or fabric is disclosed, with an optional drying step.

Drying of such surfaces or fabrics may be accomplished by any one of the common means employed either in domestic or industrial settings: machine drying or open-air drying. The fabric may comprise any fabric capable of being laundered in normal consumer or institutional use conditions, and the invention is particularly suitable for synthetic textiles such as

5 polyester and nylon and especially for treatment of mixed fabrics and/or fibres comprising synthetic and cellulosic fabrics and/or fibres. As examples of synthetic fabrics are polyester, nylon, these may be present in mixtures with cellulosic fibres, for example, polycotton fabrics. The solution typically has a pH of from 7 to 11, more usually 8 to 10.5. The compositions are typically employed at concentrations from 500 ppm to 5,000 ppm in solution. The water

10 temperatures typically range from about 5 °C to about 90 °C. The water to fabric ratio is typically from about 1:1 to about 30:1.

The adjunct ingredients in the compositions of this invention may be incorporated into the composition as the product of the synthesis generating such components, either with or without an intermediate purification step. Where there is no purification step, commonly the

15 mixture used will comprise the desired component or mixtures thereof (and percentages given herein relate to the weight percent of the component itself unless otherwise specified) and in addition unreacted starting materials and impurities formed from side reactions and/or incomplete reaction. For example, for an ethoxylated or substituted component, the mixture will likely comprise different degrees of ethoxylation/substitution.

20

### Examples

The following example formulations are suitable for use in the method of the present invention and the dosages are selected to ensure the surfactant system concentration remains within the range 0.05g/l to 1g/l in the aqueous wash solution.

25 Examples 1-7 Heavy Duty Liquid laundry detergent compositions

<u>Ingredients</u>	1	2	3	4	5	6	7
	% weight						
AE <sub>1.8</sub> S	1.52	0.51	0.25	0.87	-	-	-
AE <sub>3</sub> S	-	-	-	-	0.24	-	-
LAS	12.88	18.39	14.75	8.73	9.31	12.60	35.10
HSAS	1.00	0.50	-	-	-	-	-
AE9	0.40	0.30	0.30	0.30	-	-	-
AE8	-	-	-	-	-	-	3.90

AE7	-	-	-	-	0.25	1.40	-
C <sub>12-14</sub> dimethyl Amine Oxide	0.30	0.73	0.23	0.37	-	-	-
C <sub>12-18</sub> Fatty Acid	0.80	1.90	0.60	0.99	1.20	-	15.00
Citric Acid	2.50	3.96	1.88	1.98	0.90	2.50	0.60
Optical Brightener 1	1.00	0.80	0.10	0.30	0.05	0.50	0.001
Optical Brightener 3	0.001	0.05	0.01	0.20	0.50	-	1.00
Sodium formate	1.60	0.09	1.20	0.04	1.60	1.20	0.20
DTI 1	0.32	0.05	-	0.60	0.10	0.60	0.01
DTI 2	0.32	0.10	0.60	0.60	0.05	0.40	0.20
Sodium hydroxide	2.30	3.80	1.70	1.90	1.70	2.50	2.30
Monoethanolamine	1.40	1.49	1.00	0.70	-	-	-
Diethylene glycol	5.50	-	4.10	-	-	-	-
Chelant 1	0.15	0.15	0.11	0.07	0.50	0.11	0.80
4-formyl-phenylboronic acid	-	-	-	-	0.05	0.02	0.01
Sodium tetraborate	1.43	1.50	1.10	0.75	-	1.07	-
Ethanol	1.54	1.77	1.15	0.89	-	3.00	7.00
Polymer 1	0.10	-	-	-	-	-	2.00
Polymer 2	0.30	0.33	0.23	0.17	-	-	-
Polymer 3	-	-	-	-	-	-	0.80
Polymer 4	0.80	0.81	0.60	0.40	1.00	1.00	-
1,2-Propanediol	-	6.60	-	3.30	0.50	2.00	8.00
Structurant	0.10	-	-	-	-	-	0.10
Perfume	1.60	1.10	1.00	0.80	0.90	1.50	1.60
Perfume encapsulate	0.10	0.05	0.01	0.02	0.10	0.05	0.10
Protease	0.80	0.60	0.70	0.90	0.70	0.60	1.50
Mannanase	0.07	0.05	0.045	0.06	0.04	0.045	0.10
Amylase 1	0.30	-	0.30	0.10	-	0.40	0.10
Amylase 2	-	0.20	0.10	0.15	0.07	-	0.10
Xyloglucannase	0.20	0.10	-	-	0.05	0.05	0.20
Lipase	0.40	0.20	0.30	0.10	0.20	-	-
Polishing enzyme	-	0.04	-	-	-	0.004	-
Nuclease	0.05	0.03	0.01	0.03	0.03	0.003	0.003
Dispersin B	-	-	-	0.05	0.03	0.001	0.001

Acid Violet 50	0.05	-	-	-	-	-	0.005
Direct Violet 9	-	-	-	-	-	0.05	-
Violet DD	-	0.035	0.02	0.037	0.04	-	-
Water, dyes & minors	Balance						
pH	8.2						

Based on total cleaning and/or treatment composition weight. Enzyme levels are reported as raw material.

#### Examples 8 to 16 Unit Dose Compositions

5 These examples provide various formulations for unit dose laundry detergents. Compositions 8 to 12 comprise a single unit dose compartment. The film used to encapsulate the compositions in PVA.

<u>Ingredients</u>	<b>8</b>	<b>9</b>	<b>10</b>	<b>11</b>	<b>12</b>
	<b>% weight</b>				
LAS	28.0	31.5	33.3	29.8	33.3
AE3S	2.8	1.4	0.7	2.1	0.7
AE7	4.2	2.1	1.1	3.2	1.1
Citric Acid	0.6	0.6	0.6	0.6	0.6
C12-15 Fatty Acid	14.8	14.8	14.8	14.8	14.8
Polymer 3	4.0	4.0	4.0	4.0	4.0
Chelant 2	1.2	1.2	1.2	1.2	1.2
Optical Brightener 1	0.20	0.25	0.01	0.01	0.50
Optical Brightener 2	0.20	-	0.25	0.03	0.01
Optical Brightener 3	0.18	0.09	0.30	0.01	-
DTI 1	0.10	-	0.20	0.01	0.05
DTI 2	-	0.10	0.20	0.25	0.05
Glycerol	6.1	6.1	6.1	6.1	6.1
Monoethanol amine	8.0	8.0	8.0	8.0	8.0
Tri-isopropanol amine	-	-	2.0	-	-
Tri-ethanol amine	-	2.0	-	-	-
Cumene sulphonate	-	-	-	-	2.0
Protease	0.80	0.60	0.07	1.00	1.50

Mannanase	0.07	0.05	0.05	0.10	0.01
Amylase 1	0.20	0.11	0.30	0.50	0.05
Amylase 2	0.11	0.20	0.10	-	0.50
Polishing enzyme	0.005	0.05	-	-	-
Nuclease	0.005	0.05	0.005	0.010	0.005
Dispersin B	0.010	0.05	0.005	0.005	-
cyclohexyl dimethanol	-	-	-	2.0	-
Acid violet 50	0.03	0.02			
Violet DD			0.01	0.05	0.02
Structurant	0.14	0.14	0.14	0.14	0.14
Perfume	1.9	1.9	1.9	1.9	1.9
Water and miscellaneous			To 100%		
pH			7.5-8.2		

Based on total cleaning and/or treatment composition weight. Enzyme levels are reported as raw material.

In the following examples the unit dose has three compartments, but similar compositions can be

5 made with two, four or five compartments. The film used to encapsulate the compartments is polyvinyl alcohol.

<u>Base compositions</u>	<u>13</u>	<u>14</u>	<u>15</u>	<u>16</u>
	<u>% weight</u>			
HLAS	35.8	27.8	27.0	31.7
AE7	8.9	4.9	3.0	1.7
Citric Acid	0.5	0.7	0.6	0.5
C12-15 Fatty acid	16.4	6.0	11.0	13.0
Polymer 1	2.9	0.1	-	-
Polymer 3	1.1	5.1	2.5	4.2
Cationic cellulose polymer	-	-	0.3	0.5
Polymer 6	-	1.5	0.3	0.2
Chelant 2	1.1	2.0	0.6	1.5
Optical Brightener 1	0.20	0.25	0.01	0.005
Optical Brightener 3	0.18	0.09	0.30	0.005
DTI 1	0.1	-	0.2	-

DTI 2	-	0.1	0.2	-
Glycerol	5.3	5.0	5.0	4.2
Monoethanolamine	10.0	8.1	8.4	7.6
Polyethylene glycol	-	-	2.5	3.0
Potassium sulfite	0.2	0.3	0.5	0.7
Protease	0.80	0.60	0.40	0.80
Amylase 1	0.20	0.20	0.200	0.30
Polishing enzyme	-	-	0.005	0.005
Nuclease	0.05	0.010	0.005	0.005
Dispersin B	-	0.010	0.010	0.010
MgCl <sub>2</sub>	0.2	0.2	0.1	0.3
Structurant	0.2	0.1	0.2	0.2
Acid Violet 50	0.04	0.03	0.05	0.03
Perfume / encapsulates	0.10	0.30	0.01	0.05
Solvents and misc.	To 100%			
pH	7.0-8.2			

<b><u>Finishing compositions</u></b>	<b>17</b>			<b>18</b>		
Compartment	A	B	C	A	B	C
Volume of each compartment	40 ml	5 ml	5 ml	40 ml	5 ml	5 ml
<b><u>Ingredients</u></b>	Active material in Wt.%					
Perfume	1.6	1.6	1.6	1.6	1.6	1.6
Violet DD	0	0.006	0	0	0.004	-
TiO <sub>2</sub>	-	-	0.1	-	-	0.1
Sodium Sulfite	0.4	0.4	0.4	0.3	0.3	0.3
Polymer 5	-	-	-	2	-	-
Hydrogenated castor oil	0.14	0.14	0.14	0.14	0.14	0.14
Base Composition 13, 14, 15 or 16	Add to 100%					

Based on total cleaning and/or treatment composition weight, enzyme levels are reported as raw material.

5 Examples 19 to 24: Granular laundry detergent compositions for hand washing or washing machines, typically top-loading washing machines.

<u>Ingredient</u>	<b>19</b>	<b>20</b>	<b>21</b>	<b>22</b>	<b>23</b>	<b>24</b>
	<b>% weight</b>					
LAS	20	22	20	15	19.5	20
Quaternary ammonium	0.7	0.2	1.0	0.6	-	-
AE3S	0.9	1.0	0.9	-	0.4	0.9
AE7	-	-	-	1.0	0.1	3.0
Sodium Tripolyphosphate	5.0	-	4.0	9.0	2.0	-
Zeolite A	-	1.0	-	1.0	4.0	1.0
Sodium silicate 1.6R	7.0	5.0	2.0	3.0	3.0	5.0
Sodium carbonate	20.0	17.0	23.0	14.0	14.0	16.0
Polyacrylate MW 4500	1.0	0.6	1.0	1.0	1.5	1.0
Polymer 6	0.1	0.2	-	-	0.1	-
Carboxymethyl cellulose	1.0	0.3	1.0	1.0	1.0	1.0
Acid Violet 50	0.05	-	0.02	-	0.04	-
Violet DD	-	0.03	-	0.03	-	0.03
Protease 2	0.10	0.10	0.10	0.10	-	0.10
Amylase	0.03	-	0.03	0.03	0.03	0.03
Lipase	0.03	0.07	0.30	0.10	0.07	0.40
Polishing enzyme	0.002	-	0.05	-	0.02	-
Nuclease	0.001	0.001	0.01	0.05	0.002	0.02
Dispersin B	0.001	0.001	0.05	-	0.001	-
Optical Brightener 1	0.200	0.001	0.300	0.650	0.050	0.001
Optical Brightener 2	0.060	-	0.650	0.180	0.200	0.060
Optical Brightener 3	0.100	0.060	0.050	-	0.030	0.300
Chelant 1	0.60	0.80	0.60	0.25	0.60	0.60
DTI 1	0.32	0.15	0.15	-	0.10	0.10
DTI 2	0.32	0.15	0.30	0.30	0.10	0.20
Sodium Percarbonate	-	5.2	0.1	-	-	-
Sodium Perborate	4.4	-	3.85	2.09	0.78	3.63
Nonanoyloxy benzensulphonate	1.9	0.0	1.66	0.0	0.33	0.75
Tetraacetylenehtylenediamine	0.58	1.2	0.51	0.0	0.015	0.28
Photobleach	0.0030	0.0	0.0012	0.0030	0.0021	-

S-ACMC	0.1	0.0	0.0	0.0	0.06	0.0
Sulfate/Moisture	Balance					

Examples 25-37

Granular laundry detergent compositions typically for front-loading automatic washing machines.

<u>Ingredient</u>	<b>25</b>	<b>26</b>	<b>27</b>	<b>28</b>	<b>29</b>	<b>30</b>
	<b>% weight</b>					
LAS	9.0	10.1	10.1	10.8	10.9	10.9
AE3S	-	1.8	0.5	0.6	-	0.6
AS	0.5	-	-	-	-	-
AE7	1.2	-	0.6	-	0.6	-
Quaternary ammonium	0.5	-	-	0.3	-	-
Crystalline layered silicate	4.1	-	4.8	-	-	-
Zeolite A	5.0	-	2.0	-	2.0	2.0
Citric acid	3.0	4.0	3.0	4.0	2.5	3.0
Sodium carbonate	11.0	17.0	12.0	15.0	18.0	18.0
Sodium silicate 2R	0.08	-	0.11	-	-	-
Optical Brightener 1	-	0.25	0.05	0.01	0.10	0.02
Optical Brightener 2	-	-	0.25	0.20	0.01	0.08
Optical Brightener 3	-	0.06	0.04	0.15	-	0.05
DTI 1	0.08	-	0.04	-	0.10	0.01
DTI 2	0.08	-	0.04	0.10	0.10	0.02
Soil release agent	0.75	0.72	0.71	0.72	-	-
Acrylic /maleic acid copolymer	1.1	3.7	1.0	3.7	2.6	3.8
Carboxymethyl cellulose	0.2	1.4	0.2	1.4	1.0	0.5
Protease 3	0.20	0.20	0.30	0.15	0.12	0.13
Amylase 3	0.20	0.15	0.20	0.30	0.15	0.15
Lipase	0.05	0.15	0.10	-	-	-
Amylase 2	0.03	0.07	-	-	0.05	0.05
Cellulase 2	-	-	-	-	0.10	0.10
Polishing enzyme	0.003	0.005	0.020	-	-	-
Nuclease	0.002	0.010	0.020	0.020	0.010	0.003

Dispersin B	0.002	0.010	0.020	0.020	0.010	0.002
Tetraacetylenehtylenediamine	3.6	4.0	3.6	4.0	2.2	1.4
Sodium percabonate	13.0	13.2	13.0	13.2	16.0	14.0
Chelant 3	-	0.2	-	0.2	-	0.2
Chelant 2	0.2	-	0.2	-	0.2	0.2
MgSO <sub>4</sub>	-	0.42	-	0.42	-	0.4
Perfume	0.5	0.6	0.5	0.6	0.6	0.6
Suds suppressor agglomerate	0.05	0.10	0.05	0.10	0.06	0.05
Soap	0.45	0.45	0.45	0.45	-	-
Acid Violet 50	0.04	-	0.05	-	0.04	-
Violet DD	-	0.04	-	0.05	-	0.04
S-ACMC	0.01	0.01	-	0.01	-	-
Direct Violet 9 (active)	-	-	0.0001	0.0001	-	-
Sulfate/ Water & Miscellaneous	Balance					

AE1.8S is C<sub>12-15</sub> alkyl ethoxy (1.8) sulfate

AE3S is C<sub>12-15</sub> alkyl ethoxy (3) sulfate

5 AE7 is C<sub>12-13</sub> alcohol ethoxylate, with an average degree of ethoxylation of 7

AE8 is C<sub>12-13</sub> alcohol ethoxylate, with an average degree of ethoxylation of 8

AE9 is C<sub>12-13</sub> alcohol ethoxylate, with an average degree of ethoxylation of 9

10 Amylase 1 is Stainzyme®, 15 mg active/g

Amylase 2 is Natalase®, 29 mg active/g

Amylase 3 is Stainzyme Plus®, 20 mg active/g,

AS is C<sub>12-14</sub> alkylsulfate

15 Cellulase 2 is Celluclean™, 15.6 mg active/g

Xyloglucanase is Whitezyme®, 20mg active/g

Chelant 1 is diethylene triamine pentaacetic acid

Chelant 2 is 1-hydroxyethane 1,1-diphosphonic acid

Chelant 3 is sodium salt of ethylenediamine-N,N'-disuccinic acid, (S,S) isomer (EDDS)

20

Dispersin B	is a glycosidase hydrolase, reported as 1000mg active/g
DTI 1	is poly(4-vinylpyridine-1-oxide) (such as Chromabond S-403E®),
DTI 2	is poly(1-vinylpyrrolidone-co-1-vinylimidazole) (such as Sokalan HP56® ).
5 HSAS	is mid-branched alkyl sulfate as disclosed in US 6,020,303 and US6,060,443
LAS	is linear alkylbenzenesulfonate having an average aliphatic carbon chain length C <sub>9</sub> -C <sub>15</sub> (HLAS is acid form).
Lipase	is Lipex®, 18 mg active/g
10 Mannanase	is Mannaway®, 25 mg active/g
Nuclease	is a Phosphodiesterase SEQ ID NO 1, reported as 1000mg active/g
Optical Brightener 1	is disodium 4,4'-bis{[4-anilino-6-morpholino- <u>s</u> -triazin-2-yl]-amino}-2,2'-stilbenedisulfonate
Optical Brightener 2	is disodium 4,4'-bis-(2-sulfostyryl)biphenyl (sodium salt)
15 Optical Brightener 3	is Optiblanc SPL10® from 3V Sigma
Perfume encapsulate	is a core–shell melamine formaldehyde perfume microcapsules.
Photobleach	is a sulphonated zinc phthalocyanine
Polishing enzyme	is Paranitrobenzyl esterates, reported as 1000mg active/g
20 Polymer 1	is bis((C <sub>2</sub> H <sub>5</sub> O)(C <sub>2</sub> H <sub>4</sub> O)n)(CH <sub>3</sub> )-N <sup>+</sup> -C <sub>x</sub> H <sub>2x</sub> -N <sup>+</sup> -(CH <sub>3</sub> )-bis((C <sub>2</sub> H <sub>5</sub> O)(C <sub>2</sub> H <sub>4</sub> O)n), wherein n = 20-30,x = 3 to 8 or sulphated or sulphonated variants thereof
Polymer 2	is ethoxylated (EO <sub>15</sub> ) tetraethylene pentamine
Polymer 3	is ethoxylated polyethylenimine
Polymer 4	is ethoxylated hexamethylene diamine
25 Polymer 5	is Acusol 305, provided by Rohm&Haas
Polymer 6	is a polyethylene glycol polymer grafted with vinyl acetate side chains, provided by BASF.
Protease	is Purafect Prime®, 40.6 mg active/g
Protease 2	is Savinase®, 32.89 mg active/g
30 Protease 3	is Purafect®, 84 mg active/g
Quaternary ammonium	is C <sub>12-14</sub> Dimethylhydroxyethyl ammonium chloride
S-ACMC	is Rective Blue 19 Azo-CM-Cellulose provided by Megazyme
Soil release agent	is Repel-o-tex®
Structurant	is Hydrogenated Castor Oil

Violet DD is a thiophen azo dye provided by Milliken

- 5 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:

1. A method of treating a textile comprising (i) contacting the textile with an aqueous solution comprising a nuclease enzyme, preferably a deoxyribonuclease or ribonuclease enzyme and from 0.05g/l to 1g/l of a surfactant system, said surfactant system comprising at least 80% by weight alkyl benzene sulphonate surfactant, preferably at least 85 % by weight linear alkyl benzene sulphonate; and from 0 to 0.5g/l sodium aluminosilicate; and optionally rinsing and drying the textile.
2. A method according to any preceding claim wherein the aqueous solution comprises from 0.01ppm to 1000 ppm of the nuclease enzyme.
3. A method according to any preceding claim wherein the nuclease is selected from any of E.C. classes E.C. 3.1.21.x (where x=1, 2, 3, 4, 5, 6, 7, 8, 9), 3.1.22.y (where y=1, 2, 4, 5), E.C. 3.1.30.z (where z=1, 2) or E.C. 3.1.31.1, or mixtures thereof, preferably from E.C. 3.1.21, preferably E.C. 3.1.21.1.
4. A method according to any preceding claim wherein the nuclease enzyme comprises a deoxyribonuclease.
5. A method according to claim 5 in which the enzyme comprises an enzyme having both RNase and DNase activity, preferably being from E.C. 3.1.30.2.
6. A method according to any preceding claim wherein the enzyme is a microbial, preferably a bacterial enzyme.
7. A method according to any preceding claim wherein the enzyme has an amino acid sequence having at least 85%, or at least 90 or at least 95% or even at least 100% identity with the amino acid sequence shown in SEQ ID NO:1, SEQ ID NO:2 or SEQ ID NO:3.
8. A method according to any preceding claim wherein the composition comprises a  $\beta$ -N-acetylglucosaminidase enzyme from E.C. 3.2.1.52, preferably an enzyme having at least 70% identity to SEQ ID NO:4.
9. A method according to any preceding claim wherein the aqueous solution additionally comprises fabric shading dye and/or an additional enzyme selected from lipases, such as first wash lipases, amylases, proteases, mannanases, pectate lyases, cellulases and cutinases.
10. A method according to any preceding claim wherein the fabric in step (ii) is contacted with a laundry detergent composition in a wash cycle of an automatic washing machine and wherein the length of the wash cycle is at 3 minutes, or even at least 6 minutes, but

no more than 40 minutes, or even no more than 30 mins, or even no more than 20 minutes.

11. A method according to any preceding claims, wherein in step (ii) the fabric is contacted with a laundry cleaning and/or treatment composition in a wash cycle of an automatic washing machine and wherein the wash cycle is run at a temperature of between 5°C and 50°C, preferably between 10°C and 30°C.

# INTERNATIONAL SEARCH REPORT

International application No  
PCT/US2016/029425

**A. CLASSIFICATION OF SUBJECT MATTER**  
INV. C11D3/386  
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 practicable, 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.
X	WO 2014/087011 A1 (NOVOZYMES AS [DK]) 12 June 2014 (2014-06-12) pages 8-9; claims pages 12-13 page 1 ----- A US 6 174 852 B1 (HAYASHI HIROMITSU [JP] ET AL) 16 January 2001 (2001-01-16) column 8, line 35 - line 38; claims; examples ----- A US 2010/093595 A1 (HOLZHAUER FREDERICK W [US] ET AL) 15 April 2010 (2010-04-15) paragraph [0068]; claims ----- -/-	1-11 1-11 1-11

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 application or patent 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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
24 June 2016	05/07/2016
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**INTERNATIONAL SEARCH REPORT**

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