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(54) **Method of Laundering a Fabric**

(57) A method of laundering a fabric comprising the steps of; (i) contacting the fabric with a lipid esterase selected from class E.C. 3.1.1.3, class E.C. 3.1.1.1 , class E.C. 3.1.1.74 or a combination thereof; (ii) contacting the fabric from step (i) with a soil; (iii) contacting the fabric from step (ii) with a surfactant composition and then (iv) contacting the fabric from step (iii) with an aqueous wash liquor comprising a laundry detergent composition, wherein the laundry detergent composition optionally comprises a detersive surfactant, and optionally comprises a lipid esterase.

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Description

FIELD OF THE INVENTION

[0001] The present invention relates to methods of laundering fabrics.

BACKGROUND OF THE INVENTION

[0002] Lipid esterase enzymes are used in fabric care compositions to provide fabric cleaning benefits during the wash.

[0003] In US6265191B1, Clorox discloses a method of washing a fabric in which the fabric is washed a first time with a composition comprising a lipid esterase enzyme, and a second wash comprising a composition comprising a lipid esterase enzyme. Clorox discloses deposition of lipid esterases from E.C. class 3.1.1.74 followed by a wash cycle in which lipase and cutinase are present. The present inventors have found that whilst the lipid esterase has been found to break down soil by hydrolysis and improve cleaning, in heavily soiled/stained areas, it has been found that the break-down products of the hydrolysis reaction may build up locally into levels which cannot be fully removed in a subsequent wash step. The present invention alleviates this problem.

SUMMARY OF THE INVENTION

[0004] The present invention is to a method of laundering a fabric comprising the steps of: (i) contacting the fabric with a lipid esterase selected from class E.C. 3.1.1.3, class E.C. 3.1.1.1 or a combination thereof; (ii) contacting the fabric from step (i) with a soil; (iii) contacting the fabric from step (ii) with a surfactant composition, wherein the surfactant composition comprises from 5 to 100 wt% detersive surfactant; and (iv) contacting the fabric from step (iii) with an aqueous wash liquor comprising a detergent composition.

DETAILED DESCRIPTION OF THE INVENTION

The method

[0005] A fabric may be contacted with the lipid esterase in step (i) in a wash operation. The fabric may then be dried and worn by a consumer or used in another way for its intended use. It is during the use of the fabric that it is contacted with a soil. Following use of the fabric by the consumer the fabric is then contacted with a surfactant composition in step (iii). The surfactant composition may comprise part of a (fully formulated) laundry detergent composition, and if so, contact is with a laundry detergent composition comprising the required concentration of surfactant. Preferably this contact step of the surfactant composition is directly onto dry fabric. In contact step (iii) contact of the fabric with the surfactant composition may be with a portion of the fabric only, for example, contact may be on heavily soiled or stained portions of the fabric only. Following contact with the surfactant composition in step (iii), the fabric is then contacted with an aqueous wash liquor comprising a laundry detergent composition in step (iv). Without wishing to be bound by theory, it is believed that the lipid esterase contacted with the fabric in step (i) acts 'out of the wash' to hydrolyse lipid esters in the soil contacted to the fabric in step (ii). This effects some hydrolysis of the soil so that it is more effectively stripped from the fabric in the subsequent steps (iii) and (iv).

[0006] By 'E.C. class' we herein mean the Enzyme Commission class. The Enzyme Commission class is an international recognized enzyme classification scheme based on chemical reactions that the enzymes catalyse.

Step (i)

[0007] The method of the present invention comprises a step (i) of contacting a fabric with a lipid esterase to provide deposition of the lipid esterase onto the fabric surface. Any contact method may be used however, typically contact is effected by forming an aqueous liquor comprising the lipid esterase and contacting that with the fabric, for example by immersion of the fabric in the aqueous liquor. Preferably, the lipid esterase is contacted with the fabric in an aqueous step in which an aqueous wash liquor comprising the lipid esterase is contacted with the fabric. For example the wash liquor may be prepared by addition of a laundry detergent composition comprising a lipid esterase and additional detergent ingredient(s) to water or by addition of a laundry detergent composition substantially free of the lipid esterase to water with further addition of the lipid esterase essential for step (i), to form aqueous wash liquor. The aqueous wash liquor may be formed in a wash cycle of a machine wash operation or in a hand-washing step. Alternatively, the lipid esterase may be added to the fabric in the form of a pre-treater. For example it may be deposited as a pre-treat stain remover composition. In this aspect, the pre-treat composition is added to a portion or all of the fabric or to a specific stain on the fabric. Alternatively the lipid esterase may be deposited on the fabric during fabric manufacture. The lipid esterase may

be added to water to form an aqueous wash liquor by the addition of a lipid-esterase-containing laundry detergent composition with water.

[0008] The lipid esterase is selected from class E.C. 3.1.1.3, class E.C. 3.1.1. or a combination thereof. The lipid esterase may be selected from class E.C.3.1.1.3. The lipid esterase may be selected from class E.C. 3.1.1.1

[0009] The lipid esterase may be a variant having at least 90% sequence identity to wild-type lipase from *Thermomyces lanuginosus* and having sequence substitutions T231R and N233R.

[0010] E.C class 3.1.1.3 includes Triacylglycerol lipases. Suitable triacylglycerol lipases can be selected from variants of the *Humicola lanuginosa (Thermomyces lanuginosus)* lipase. Other suitable triacylglycerol lipases can be selected from variants of *Pseudomonas lipases,* e.g., from *P. alcaligenes* or *P. pseudoalcaligenes* (EP 218 272), *P. cepacia* (EP 331 376), *P. stutzeri* (GB 1,372,034), *P. fluorescens, Pseudomonas* sp. strain SD 705 (WO 95/06720 and WO 96/27002), *P. wisconsinensis* (WO 96/12012), *Bacillus* lipases, e.g., from *B. subtilis* (Dartois et al. (1993), Biochemica et Biophysica Acta, 1131, 253-360), *B. stearothermophilus* (JP 64/744992) or *B. pumilus* (WO 91/16422).

[0011] E.C class 3.1.1.1. includes Carboxylic ester hydrolases. Suitable carboxylic ester hydrolases can be selected from wild-types or variants of carboxylic ester hydrolases endogenous to *B. gladioli, P. fluorescens, P. putida, B. acidocaldarius, B. subtilis, B. stearothermophilus, Streptomyces chrysomallus, S. diastatochromogenes and Saccaromyces cerevisiae.*

[0012] In step (i), the fabric may be contacted with a lipid esterase at a concentration of between 30 and 2000 ng enzyme/g fabric. Alternatively, the fabric may be contacted with a lipid esterase at a concentration of between 50 and 1700ng enzyme/g fabric, or even 80 and 1600ng enzyme/g fabric. Without wishing to be bound by theory, it is believed that these concentrations are optimal for soil removal from the fabrics.

[0013] In step (i), the fabric may also be contacted with a detersive surfactant, thus in a preferred embodiment contact comprises contacting an aqueous liquor comprising the lipid esterase and additionally a surfactant. Suitable surfactant or mixtures of surfactants (surfactant compositions) are described below. A particularly preferred surfactant composition comprises alkyl alkoxylated sulfate surfactant. Without wishing to be bound by theory, it is believed that the presence of the detersive surfactant improved the stability of the lipid esterase through the wash. The presence of the detersive surfactant also improved deposition of the lipid esterase onto the fabrics and assisted in providing a higher concentration of deposited lipid esterase being in the correct orientation on the fabric to be catalytically active.

[0014] The fabric may be any suitable fabric. The fabric may comprise natural or synthetic materials or a combination thereof. The fabric may comprise cotton, polycotton, polyester, or a combination thereof. The fabric may comprise cotton. The pre-deposited lipid esterase may reduce the adherence of a soil already on the fabric prior to deposition of the lipid esterase, or one in which a soil is applied to the fabric following deposition of the lipid esterase onto the fabric and hydrolyses soils on the fabric surface. Since adherence of the soil to the fabric is reduced and/or the soil is broken down, the ability to remove the soil is improved as compared to the prior art. However, localized areas of hydrolysis products of the soil may be difficult to remove in a subsequent wash step. A preferred ratio of detersive surfactant to fabric on a weight to weight basis in step (i) may be from 1:150 to 1:500.

[0015] The lipid esterase in step (i) can be contacted with the fabric in combination with any other known laundry detergent ingredients detailed below, for example in a fully formulated laundry detergent composition comprising the lipid esterase essential in step (i). Following contact of the fabric with the lipid esterase, the fabric is preferably dried prior to step (ii).

Step (ii)

[0016] The method of the present invention comprises a step (ii) of contacting the fabric from step (i) with a soil. By 'soil' we mean herein any organic or inorganic material that is deposited onto the fabric that the consumer perceives as dirtying the fabric. The soil could be a stain, for example a greasy or oily food stain, or body soils such as sweat or blood. Other common stains include red food stains, clay-based stains and grass stains. Alternatively, the soil could be atmospheric soil such as chemical pollutants, dust or soot. The soil may be water-soluble or water-insoluble. These are non-limiting examples. Those skilled in the art would know what is meant by 'soil' in the context of the present invention. Contact of the fabric with a soil takes place in the normal use of the fabric article, for example by wearing fabric garments or typical consumer use of other fabric articles.

Step (iii)

[0017] The fabric from step (ii) is contacted with a surfactant composition comprising from 5 to 100 wt% detersive surfactant. The surfactant composition may comprise at least 10 or 15 or even at least 20 wt% surfactant. Typically the surfactant composition comprises up to 90 or 80 or 70 or 60 or even 50 wt% surfactant. The surfactant composition may be provided by a laundry detergent composition comprising the required concentration of surfactant. Where the surfactant composition is provided by a laundry detergent composition, additional laundry detergent adjuncts will be present in

addition to the essential detersive surfactant, as described below. In a preferred embodiment of the invention the surfactant composition comprises no more than 70 wt% water or no more than 60 or 50 or 40 or 30 or 20 or 10 wt% water. In a preferred embodiment the surfactant composition is a liquid detergent composition, preferably a fully formulated liquid detergent composition suitable for addition to water for a wash step. In step (iii) preferably contact of the fabric with the surfactant composition is directly onto dry fabric, however a pre-wetting step may be introduced. Contact with the surfactant composition may be with only a portion of the fabric surface, for example onto a heavily soiled/stained portion of the fabric. Contact of the fabric with the surfactant composition may be via a pretreating device which may or may not also apply friction or abrasion at the fabric surface simultaneously or subsequent to the contact of the surfactant composition with the fabric. Suitable devices are known as pre-treat devices and are often sold with laundry detergent compositions, in particular liquid laundry detergent compositions. Examples are disclosed for example in US5887753 and WO2002/07962, WO2002/07963 and WO2002/079366-70.

[0018] The detersive surfactant may be an anionic, cationic, non-ionic, zwitterionic, amphoteric surfactant or a combination thereof. The surfactant composition may comprise one surfactant or typically mixtures of more than one surfactant.

[0019] Preferably the surfactant composition comprises at least 5 wt%, more preferably at least 10 wt% anionic surfactant. Preferred anionic detersive surfactants are alkyl benzene sulfonates, alkoxylated anionic surfactant, or a combination thereof. Suitable anionic detersive surfactants include sulphate and sulphonate detersive surfactants.

[0020] Particularly preferred alkyl benzene sulphonates are linear alkylbenzene sulphonates, particularly those having a carbon chain length of C8-15, or C_{10}-$_{13}$ alkyl benzene sulphonate. Suitable alkyl benzene sulphonate (LAS) is obtainable, or even 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®. Another suitable anionic detersive surfactant is alkyl benzene sulphonate that is obtained by DETAL catalyzed process, preferably having 8 to 15 carbon atoms. Other synthesis routes, such as HF, may also be suitable.

[0021] Suitable sulphate detersive surfactants include alkyl sulphate, such as C_{8-18} alkyl sulphate, or predominantly C_{12} alkyl sulphate. The alkyl sulphate may be derived from natural sources, such as coco and/or tallow. Alternatively, the alkyl sulphate may be derived from synthetic sources such as C_{12-15} alkyl sulphate.

[0022] It may be preferred for the surfactant composition to comprise in addition an alkyl alkoxylated sulphate, such as alkyl ethoxylated sulphate, or a C_{8-18} alkyl alkoxylated sulphate, or a C_{8-18} alkyl ethoxylated sulphate. Preferably the alkyl chain length may be from 12 to 16 carbon atoms. The alkyl alkoxylated sulphate may have an average degree of alkoxylation of from 0.5 to 20, or from 0.5 to 10, or from 0.5 to 7, or from 0.5 to 5 or from 0.5 to 3. Examples include predominantly C12 sodium lauryl ether sulphate ethoxylated with an average of 3 moles of ethylene oxide per mole.

[0023] The alkyl sulphate, alkyl alkoxylated sulphate and alkyl benzene sulphonates may be linear or branched, substituted or un-substituted.

[0024] The anionic detersive surfactant may be a mid-chain branched anionic detersive surfactant, such as a mid-chain branched alkyl sulphate and/or a mid-chain branched alkyl benzene sulphonate. The mid-chain branches are typically C_{1-4} alkyl groups, such as methyl and/or ethyl groups.

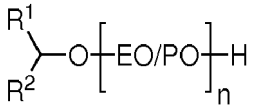
[0025] Another suitable anionic detersive surfactant is alkyl ethoxy carboxylate.

[0026] The anionic surfactants are typically present in their salt form, typically being complexed with a suitable cation. Suitable counter-ions include Na^+ and K^+, substituted ammonium such as C_1-C_6 alkanolammnonium such as monoethanolamine (MEA) tri-ethanolamine (TEA), diethanolamine (DEA), and any mixture thereof.

[0027] Preferably the surfactant composition comprises a non-ionic detersive surfactant in addition to the anionic surfactant. Preferred nonionic surfactants are primary and secondary alcohol alkoxylates, especially ethoxylates. Suitable non-ionic detersive surfactants include alkyl alkoxylated alcohols, such as C_{8-18} alkyl alkoxylated alcohol, or a C_{8-18} alkyl ethoxylated alcohol. The alkyl alkoxylated alcohol may have an average degree of alkoxylation of from 0.5 to 50, or from 1 to 30, or from 1 to 20, or from 1 to 10. The alkyl alkoxylated alcohol may be a C_{8-18} alkyl ethoxylated alcohol, typically having an average degree of ethoxylation of from 1 to 10, or from 1 to 7, or from 1 to 5, or from 3 to 7. The alkyl alkoxylated alcohol can be linear or branched, and substituted or un-substituted.

[0028] Suitable examples of nonionic surfactants include those selected from the group consisting of: C_8-C_{18} alkyl ethoxylates, such as, NEODOL® non-ionic surfactants from Shell; C_6-C_{12} alkyl phenol alkoxylates wherein optionally the alkoxylate units are ethyleneoxy units, propyleneoxy units or a mixture thereof; C_{12}-C_{18} alcohol and C_6-C_{12} alkyl phenol condensates with ethylene oxide/propylene oxide block polymers such as Pluronic® from BASF; C_{14}-C_{22} mid-chain branched alcohols; C_{14}-C_{22} mid-chain branched alkyl alkoxylates, typically having an average degree of alkoxylation of from 1 to 30; alkylpolysaccharides, such as alkylpolyglycosides; polyhydroxy fatty acid amides; ether capped poly(oxyalkylated) alcohol surfactants; and mixtures thereof. Suitable non-ionic detersive surfactants are also alkyl polyglucoside and/or an alkyl alkoxylated alcohol.

[0029] Suitable nonionic detersive surfactants include secondary alcohol-based detersive surfactants having the formula:



wherein R^1 = linear or branched, substituted or unsubstituted, saturated or unsaturated C_{2-8} alkyl; wherein R^2 = linear or branched, substituted or unsubstituted, saturated or unsaturated C_{2-8} alkyl, wherein the total number of carbon atoms present in $R^1 + R^2$ moieties is in the range of from 7 to 13; wherein EO/PO are alkoxy moieties selected from ethoxy, propoxy, or mixtures thereof, optionally the EO/PO alkoxyl moieties are in random or block configuration; wherein n is the average degree of alkoxylation and is in the range of from 4 to 10.

[0030] Other suitable non-ionic detersive surfactants include EO/PO block co-polymer surfactants, such as the Plurafac® series of surfactants available from BASF, and sugar-derived surfactants such as alkyl N-methyl glucose amide.

[0031] The ratio of anionic surfactant to nonionic surfactant may be from 2:1 to 1:2, or even from 1:1 to 1:3 or from greater than 1:1 to 1:2.

[0032] The composition may also comprise an amine oxide preferably in amounts up to 10 wt% of the surfactant composition. Suitable amine oxides are described in WO2014/114570, a particularly preferred amine oxide comprising lauryl dimethylamine oxide. The composition may also comprise a zwitterionic surfactant. A preferred zwitterionic surfactant is a betaine surfactant, for example a carbobetaine, such as Empigen® from Huntsman. Where amine oxide and/or betaine surfactant is present, the weight ratio of anionic and/or nonionic surfactant to amine oxide and/or betaine is typically from 10:1 to 20:1.

Step (iv)

[0033] The method of the present invention comprises a step (iv) of contacting the fabric from step (iii) with an aqueous wash liquor comprising a laundry detergent composition. The composition may be in any suitable form including granular, liquid or unitized dose. When in unitized dose form, it is preferred that the composition is enclosed with a water-soluble film, for example a polyvinyl alcohol-based film.

[0034] The fabric may be contacted with the composition in step (iv) in the form of a wash liquor, or even a wash liquor in a machine wash cycle.

[0035] The laundry detergent composition typically comprises from 1 to 70 wt%, or from 2 to 50 wt% or from 5 to 40 wt%, based on the total weight of the laundry detergent composition, of a surfactant. Suitable detersive surfactants comprise the surfactant composition as described in step (iii) above. Any ratio or concentration of detersive surfactants detailed above applies also to the detersive surfactant of step (iv). The concentration of the surfactant in the wash liquor is typically from 0.05 to 5g/l, or from 0.1 to 4g/l.

[0036] The laundry detergent composition may comprise a lipid esterase. The lipid esterase can be any lipid esterase. The lipid esterase may be a lipase, or a cutinase, or a combination thereof.

[0037] The lipid esterase may be selected from the following:

(1) Triacylglycerol lipases (E.C. 3.1.1.3)
(2) Carboxylic ester hydrolase (E.C. 3.1.1.1)
(3) Cutinase (E.C. 3.1.1.74)
(4) Sterol esterase (E.C. 3.1.1.13)
(5) Wax-ester hydrolase (E.C. 3.1.1.50)

[0038] Suitable triacylglycerol lipases can be selected from variants of the *Humicola lanuginosa (Thermomyces lanuginosus)* lipase. Other suitable triacylglycerol lipases can be selected from variants of *Pseudomonas lipases,* e.g., from *P. alcaligenes* or *P. pseudoalcaligenes* (EP 218 272), *P. cepacia* (EP 331 376), *P. stutzeri* (GB 1,372,034), *P. fluorescens, Pseudomonas* sp. strain SD 705 (WO 95/06720 and WO 96/27002), *P. wisconsinensis* (WO 96/12012), *Bacillus* lipases, e.g., from *B. subtilis* (Dartois et al. (1993), Biochemica et Biophysica Acta, 1131, 253-360), *B. stearothermophilus* (JP 64/744992) or *B. pumilus* (WO 91/16422).

[0039] Suitable carboxylic ester hydrolases can be selected from wild-types or variants of carboxylic ester hydrolases endogenous to *B. gladioli, P. fluorescens, P. putida, B. acidocaldarius, B. subtilis, B. stearothermophilus, Streptomyces chrysomallus, S. diastatochromogenes and Saccaromyces cerevisiae.*

[0040] Suitable cutinases can be selected from wild-types or variants of cutinases endogenous to strains of *Aspergillus,* in particular *Aspergillus oryzae,* a strain of *Alternaria,* in particular *Alternaria brassiciola,* a strain of *Fusarium,* in particular *Fusarium solani, Fusarium solani pisi, Fusarium oxysporum, Fusarium oxysporum cepa, Fusarium roseum culmorum,* or *Fusarium roseum sambucium,* a strain of *Helminthosporum,* in particular *Helminthosporum sativum,* a strain of *Humicola,* in particular *Humicola insolens,* a strain of *Pseudomonas,* in particular *Pseudomonas mendocina,* or *Pseu-*

domonas putida, a strain of *Rhizoctonia,* in particular *Rhizoctonia solani,* a strain of *Streptomyces,* in particular *Streptomyces scabies,* a strain of *Coprinopsis,* in particular *Coprinopsis cinerea,* a strain of *Thermobifida,* in particular *Thermobifida fusca,* a strain of *Magnaporthe,* in particular *Magnaporthe grisea,* or a strain of *Ulocladium,* in particular *Ulocladium consortiale.*

[0041] In a preferred embodiment, the cutinase is selected from variants of the *Pseudomonas mendocina* cutinase described in WO 2003/076580 (Genencor), such as the variant with three substitutions at I178M, F180V, and S205G.

[0042] In another preferred embodiment, the cutinase is a wild-type or variant of the six cutinases endogenous to *Coprinopsis cinerea* described in H. Kontkanen et al, App. Environ. Microbiology, 2009, p2148-2157

[0043] In another preferred embodiment, the cutinase is a wild-type or variant of the two cutinases endogenous to *Trichoderma reesei* described in WO2009007510 (VTT).

[0044] In a most preferred embodiment the cutinase is derived from a strain of *Humicola insolens,* in particular the strain *Humicola insolens* DSM 1800. *Humicola insolens* cutinase is described in WO 96/13580 which is hereby incorporated by reference. The cutinase may be a variant, such as one of the variants disclosed in WO 00/34450 and WO 01/92502. Preferred cutinase variants include variants listed in Example 2 of WO 01/92502. Preferred commercial cutinases include Novozym 51032 (available from Novozymes, Bagsvaerd, Denmark).

[0045] Suitable sterol esterases may be derived from a strain of *Ophiostoma,* for example *Ophiostoma piceae,* a strain of *Pseudomonas,* for example *Pseudomonas aeruginosa,* or a strain of *Melanocarpus,* for example *Melanocarpus albomyces.*

[0046] In a most preferred embodiment the sterol esterase is the *Melanocarpus albomyces* sterol esterase described in H. Kontkanen et al, Enzyme Microb Technol., 39, (2006), 265-273.

[0047] Suitable wax-ester hydrolases may be derived from *Simmondsia chinensis.* The lipid esterase may be selected from an enzyme in E.C. class 3.1 or 3.2 or a combination thereof. The lipid esterase may be selected from an enzyme in E.C. class 3.1.1.1 or 3.1.1.3 or a combination thereof.

[0048] It should be noted that a distinction may be drawn between the lipid esterase comprised in step (i) and any lipid esterase optionally comprised in the composition of step (iii) and/or (iv). The lipid esterase comprised in step (i) must be from E.C. classes 3.1.1.1, 3.1.1.3 or combinations thereof. The lipid esterase comprised in step (iii) and/or (iv) may be any lipid esterase and may be the same or different from the enzyme present in step (i). Without wishing to be bound by theory, it is believed that it is the specific choice of this narrow selection of enzyme in step (i) that provides improved fabric soil removal benefit.

[0049] The present invention is particularly beneficial when the soiled fabrics are washed at lower temperatures and at lower wash cycle times. There is a tendency for consumers to wash fabrics at lower temperatures and for shorter wash cycles. This is more environmentally friendly and reduces energy consumption. However, colder temperatures and short wash cycles tend to remove less soil than higher temperatures and longer wash cycles. Thus, there is a need in the art for methods of effectively removing soil from fabrics at this lower temperatures and shorter wash cycles. It was surprisingly found that the method of the present invention providing excellent soil removal from fabrics at lower temperatures. It was also surprisingly found that the method of the present invention provided excellent soil removal from fabrics in shorter wash cycles.

[0050] The fabric may be contacted with the composition in any of the steps above at a temperature of 60°C or less, or even 40°C or less. The fabric may be contacted with the composition at a temperature of between 5°C and 50°C, preferably between 10°C and 30°C. In particular in step(iii) and/or step (iv), the temperature may be no greater than 40°C or 30°C or 25°C. The fabric may be contacted at these temperatures in the wash cycle of a domestic washing machine.

[0051] The fabric may be contacted with a laundry detergent composition in step(i) and/or step (iv) in a wash cycle of an automatic washing machine and the length of the wash cycle may be at least 30 seconds, or even at least 3 mins, or even at least 6 mins, but no more than 30 mins, or even no more than 45 mins, or even no more than 1 hour.

[0052] In step (i) and/or step (iv) where the contact is in a method of laundering, the method of laundering fabric typically comprises the step of contacting the composition to water to form a wash liquor, and laundering fabric in said wash liquor, wherein typically the wash liquor has a temperature of above 0°C to 90°C, or to 60°C, or to 40°C, or to 30°C, or to 20°C, or to 10°C, or even to 8°C. The fabric may be contacted to the water prior to, or after, or simultaneous with, contacting the laundry detergent composition with water. The composition can be used in pre-treatment applications.

[0053] Typically, the wash liquor is formed by contacting the laundry detergent composition with water in such an amount that the concentration of laundry detergent composition in the wash liquor is from above 0g/l to 6g/l, or from 0.05g/l, and to 5g/l, or to 4.5g/l, or to 3.5g/l, or to 3.0g/l, or to 2.5g/l, or even to 2.0g/l, or even to 1.5g/l.

[0054] The method of laundering steps 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.

[0055] 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.

[0056] Typically from 0.01kg to 2kg of fabric per litre of wash liquor is dosed into said wash liquor. Typically from 0.01kg, or from 0.05kg, 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.

[0057] 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 laundry detergent composition is contacted with water to form the wash liquor.

[0058] There may be optional rinse and drying steps between steps (i) and (ii), (ii) and (iii) and (iii) and (iv), in particular between steps (i) and (ii). Preferably there is no rinse step between steps (iii) and (iv).

Other ingredients

[0059] The laundry detergent composition as mentioned in any of the steps above may comprise further laundry detergent ingredients. The laundry detergent composition of step may comprise a hueing agent, a polymer or a combination thereof. Suitable detergent ingredients include: hueing agent; detersive surfactants including anionic detersive surfactants, non-ionic detersive surfactants, cationic detersive surfactants, zwitterionic detersive surfactants, amphoteric detersive surfactants, and any combination thereof; polymers including carboxylate polymers, polyethylene glycol polymers, polyester soil release polymers such as terephthalate polymers, amine polymers, cellulosic polymers, dye transfer inhibition polymers, dye lock polymers such as a condensation oligomer produced by condensation of imidazole and epichlorhydrin, optionally in ratio of 1:4:1, hexamethylenediamine derivative polymers, and any combination thereof; builders including zeolites, phosphates, citrate, and any combination thereof; buffers and alkalinity sources including carbonate salts and/or silicate salts; fillers including sulphate salts and bio-filler materials; bleach including bleach activators, sources of available oxygen, pre-formed peracids, bleach catalysts, reducing bleach, and any combination thereof; chelants; photobleach; hueing agents; brighteners; enzymes including proteases, amylases, cellulases, lipases, xyloglucanases, pectate lyases, mannanases, bleaching enzymes, cutinases, and any combination thereof; fabric softeners including clay, silicones, quaternary ammonium fabric-softening agents, and any combination thereof; flocculants such as polyethylene oxide; perfume including starch encapsulated perfume accords, perfume microcapsules, perfume loaded zeolites, schif base reaction products of ketone perfume raw materials and polyamines, blooming perfumes, and any combination thereof; aesthetics including soap rings, lamellar aesthetic particles, geltin beads, carbonate and/or sulphate salt speckles, coloured clay, and any combination thereof: and any combination thereof.

[0060] Fabric Hueing Agents - The composition may comprise a fabric hueing agent (sometimes referred to as shading, bluing or whitening agents). Typically the hueing agent provides a blue or violet shade to fabric. Hueing agents 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. Hueing agents 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 hueing agents include dyes, dye-clay conjugates, and organic and inorganic pigments. Suitable dyes include small molecule dyes and polymeric dyes. Suitable small molecule dyes include small molecule dyes selected from the group consisting of dyes falling into the Colour Index (C.I.) classifications of Acid, Direct, Basic, Reactive or hydrolysed 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. 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 9, 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, 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, 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, Direct Blue 71, Direct Violet 51, Direct Blue 1, Acid Red 88, Acid Red 150, Acid Blue 29, Acid Blue 113 or mixtures thereof.

[0061] Preferred dyes include dye polymers, wherein a dye group is bound to a polymeric group, optionally via a linking group. Suitable polymeric groups include (1) alkoxylated polyethyleneimine (for example as disclosed in WO012119859), (2) polyvinyl alcohol (for example as disclosed in WO2012130492), or (3) diamine derivative of an alkylene oxide capped polyethylene glycol (for example as disclosed in WO2012126665, especially figure 24), or polyalkoxylated alcohol, for example as described in WO2011/011799, WO2012/054058, WO2012/166699 or WO2012/166768. One preferred class

of dye polymers is obtainable by reacting a blue or violet dye containing an NH2 group with a polymer to form a covalent bond via the reacted NH2 group of the blue or violet dye and the dye polymer has an average of from 0 to 30, preferably 2 to 20, most preferably 2 to 15 repeating same units. In a preferred embodiment the monomeric units are selected from alkylene oxides, preferably ethylene oxides. Typically dye polymers will be in the form of a mixture of dye polymers in which there is a mixture of molecules having a distribution of number of monomer groups in the polymer chains, such as the mixture directly produced by the appropriate organic synthesis route, for example in the case of alkylene oxide polymers, the result of an alkoxylation reaction. Such dye polymers are typically blue or violet in colour, to give to the cloth a hue angle of 230 to 345, more preferably 250 to 330, most preferably 270 to 300. In the synthesis of dye polymers unbound blue or violet organic dyes may be present in a mixture with the final dye-polymer product. The chromophore of the blue or violet dye is preferably selected from the group consisting of: azo; anthraquinone; phthalocyanine; triphen-dioxazine; and, triphenylmethane. In one aspect the dye polymer is obtainable by reacting a dye containing an NH[2] group with a polymer or suitable monomer that forms a polymer in situ. Preferably the NH[2] is covalently bound to an aromatic ring of the dye. Unbound dye is formed when the dye does not react with polymer. Preferred dyes containing -NH[2] groups for such reactions are selected from: acid violet 1 ; acid violet 3; acid violet 6; acid violet 1 1 ; acid violet 13; acid violet 14; acid violet 19; acid violet 20; acid violet 36; acid violet 36:1 ; acid violet 41 ; acid violet 42; acid violet 43; acid violet 50; acid violet 51 ; acid violet 63; acid violet 48; acid blue 25; acid blue 40; acid blue 40:1; acid blue 41 ; acid blue 45; acid blue 47; acid blue 49; acid blue 51 ; acid blue 53; acid blue 56; acid blue 61 ; acid blue 61 :1 ; acid blue 62; acid blue 69; acid blue 78; acid blue 81 :1 ; acid blue 92; acid blue 96; acid blue 108; acid blue 1 1 1 ; acid blue 215; acid blue 230; acid blue 277; acid blue 344; acid blue 1 17; acid blue 124; acid blue 129; acid blue 129:1 ; acid blue 138; acid blue 145; direct violet 99; direct violet 5; direct violet 72; direct violet 16; direct violet 78; direct violet 77; direct violet 83; food black 2; direct blue 33; direct blue 41 ; direct blue 22; direct blue 71 ; direct blue 72; direct blue 74; direct blue 75; direct blue 82; direct blue 96; direct blue 1 10; direct blue 1 1 1 ; direct blue 120; direct blue 120:1 ; direct blue 121 ; direct blue 122; direct blue 123; direct blue 124; direct blue 126; direct blue 127; direct blue 128; direct blue 129; direct blue 130; direct blue 132; direct blue 133; direct blue 135; direct blue 138; direct blue 140; direct blue 145; direct blue 148; direct blue 149; direct blue 159; direct blue 162; direct blue 163; food black 2; food black 1 wherein the acid amide group is replaced by NH[2]; Basic Violet 2; Basic Violet 5; Basic Violet 12; Basic Violet 14; Basic Violet 8; Basic Blue 12; Basic Blue 16; Basic Blue 17; Basic Blue 47; Basic Blue 99; disperse blue 1 ; disperse blue 5; disperse blue 6; disperse blue 9; disperse blue 1 1 ; disperse blue 19; disperse blue 20; disperse blue 28; disperse blue 40; disperse blue 56; disperse blue 60; disperse blue 81 ; disperse blue 83; disperse blue 87; disperse blue 104; disperse blue 1 18; disperse violet 1 ; disperse violet 4, disperse violet 8, disperse violet 17, disperse violet 26; disperse violet 28; solvent violet 26; solvent blue 12; solvent blue 13; solvent blue 18; solvent blue 68. Further preferred dyes are selected from mono-azo dyes which contain a phenyl group directly attached to the azo group, wherein the phenyl group has an NH[2] groups covalent bound to it. For example a mono-azo thiophene dye. The polymer chain may be selected from polyalkylene oxides. The polymer chain andf/or the dye chromophore group may optionally carry anionic or cationic groups. Examples of polyoxyalkylene oxide chains include ethylene oxide, propylene oxide, glycidol oxide, butylene oxide and mixtures thereof.

[0062] 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, US 7,686,892 B2, and WO2010/142503.

[0063] In another aspect, suitable polymeric dyes include polymeric dyes selected from the group consisting of fabric-substantive colorants sold under the name of Liquitint® (Milliken, Spartanburg, South Carolina, USA), dye-polymer conjugates formed from at least one reactive dye and a polymer selected from the group consisting of polymers comprising a moiety selected from the group consisting of a hydroxyl moiety, a primary amine moiety, a secondary amine moiety, a thiol moiety and mixtures thereof. In still another aspect, suitable polymeric dyes include polymeric dyes selected from the group consisting of Liquitint® Violet CT, carboxymethyl cellulose (CMC) covalently bound to a reactive blue, reactive violet or reactive red dye such as CMC conjugated with C.I. Reactive Blue 19, sold by Megazyme, Wicklow, Ireland under the product name AZO-CM-CELLULOSE, product code S-ACMC, alkoxylated triphenyl-methane polymeric colourants, alkoxylated thiophene polymeric colourants, and mixtures thereof.

[0064] Preferred hueing dyes include the whitening agents found in WO 08/87497 A1, 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 8,138,222B2, especially claim 1 of US 8,138,222B2. Other preferred dyes are disclosed in US 7,909,890 B2.

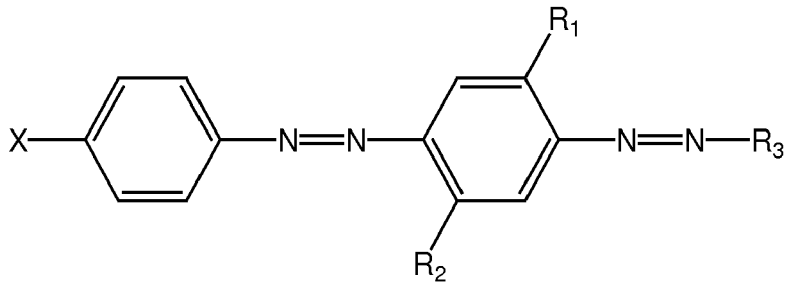
[0065] Suitable dye clay conjugates include dye clay conjugates selected from the group comprising at least one cationic/basic dye and a smectite clay, and mixtures thereof. In another aspect, suitable dye clay conjugates include dye clay conjugates selected from the group consisting of one cationic/basic dye selected from the group consisting of C.I. Basic Yellow 1 through 108, C.I. Basic Orange 1 through 69, C.I. Basic Red 1 through 118, C.I. Basic Violet 1 through

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

[0066] Suitable pigments include pigments selected from the group consisting of flavanthrone, indanthrone, chlorinated indanthrone containing from 1 to 4 chlorine atoms, pyranthrone, dichloropyranthrone, monobromodichloropyranthrone, dibromodichloropyranthrone, tetrabromopyranthrone, perylene-3,4,9,10-tetracarboxylic acid diimide, wherein the imide groups may be unsubstituted or substituted by C1-C3 -alkyl or a phenyl or heterocyclic radical, and wherein the phenyl and heterocyclic radicals may additionally carry substituents which do not confer solubility in water, anthrapyrimidine-carboxylic acid amides, violanthrone, isoviolanthrone, dioxazine pigments, copper phthalocyanine which may contain up to 2 chlorine atoms per molecule, polychloro-copper phthalocyanine or polybromochloro-copper phthalocyanine containing up to 14 bromine atoms per molecule and mixtures thereof.

[0067] In another aspect, suitable pigments include pigments selected from the group consisting of Ultramarine Blue (C.I. Pigment Blue 29), Ultramarine Violet (C.I. Pigment Violet 15) and mixtures thereof.

[0068] The hueing agent may having the following structure:



wherein:

R_1 and R_2 are independently selected from the group consisting of: H; alkyl; alkoxy; alkyleneoxy; alkyl capped alkyleneoxy; urea; and amido;

R_3 is a substituted aryl group;

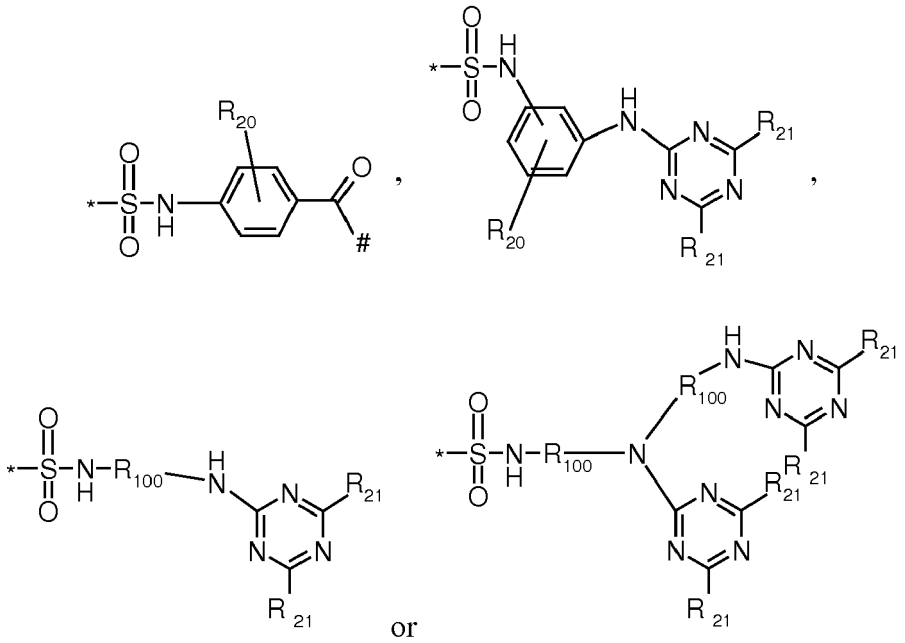
X is a substituted group comprising sulfonamide moiety and optionally an alkyl and/or aryl moiety, and wherein the substituent group comprises at least one alkyleneoxy chain that comprises at least four alkyleneoxy moieties.

[0069] The hueing agent may comprise

a) a Zn-, Ca-, Mg-, Na-, K-, A1, Si-, Ti-, Ge-, Ga-, Zr-, In- or Sn- phthalocyanine compound of formula (1)

(PC)-L-(D) (1)

to which at least one mono-azo dyestuff is attached through a covalent bonding via a linking group L wherein
PC is a metal-containing phthalocyanine ring system;
D is the radical of a mono-azo dyestuff; and
L is a group



wherein
R_{20} is hydrogen, C_1- C_8alkyl, C_1-C_8alkoxy or halogen;
R_{21} is independently D, hydrogen, OH, Cl or F, with the proviso that at least one is D;
R_{100} is C_1-C_8alkylene
* is the point of attachment of PC;
# is the point of attachment of the dye.

[0070] The aforementioned fabric hueing agents can be used in combination (any mixture of fabric hueing agents can be used).

[0071] **Cationic detersive surfactant:** Suitable cationic detersive surfactants include alkyl pyridinium compounds, alkyl quaternary ammonium compounds, alkyl quaternary phosphonium compounds, alkyl ternary sulphonium compounds, and mixtures thereof.

[0072] Suitable cationic detersive surfactants are quaternary ammonium compounds having the general formula:

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

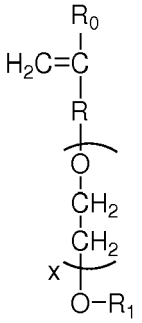
wherein, R is a linear or branched, substituted or unsubstituted C_{6-18} alkyl or alkenyl moiety, R_1 and R_2 are independently selected from methyl or ethyl moieties, R_3 is a hydroxyl, hydroxymethyl or a hydroxyethyl moiety, X is an anion which provides charge neutrality, suitable anions include: halides, such as chloride; sulphate; and sulphonate. Suitable cationic detersive surfactants are mono-C_6-$_{18}$ alkyl mono-hydroxyethyl di-methyl quaternary ammonium chlorides. Suitable cationic detersive surfactants are mono-C_{8-10} alkyl mono-hydroxyethyl di-methyl quaternary ammonium chloride, mono-C_{10-12} alkyl mono-hydroxyethyl di-methyl quaternary ammonium chloride and mono-C_{10} alkyl mono-hydroxyethyl di-methyl quaternary ammonium chloride.

[0073] **Polymer:** Suitable polymers include carboxylate polymers, polyethylene glycol polymers, polyester soil release polymers such as terephthalate polymers, amine polymers, cellulosic polymers, dye transfer inhibition polymers, dye lock polymers such as a condensation oligomer produced by condensation of imidazole and epichlorhydrin, optionally in ratio of 1:4:1, hexamethylenediamine derivative polymers, and any combination thereof.

[0074] **Carboxylate polymer:** 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.

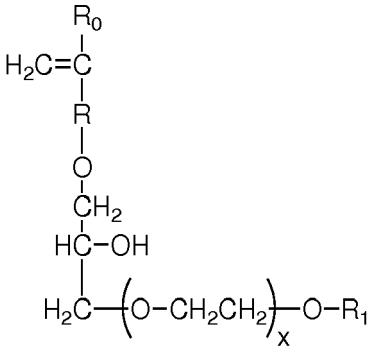
[0075] Other suitable carboxylate polymers are co-polymers comprising: (i) from 50 to less than 98 wt% structural units derived from one or more monomers comprising carboxyl groups; (ii) from 1 to less than 49 wt% structural units derived from one or more monomers comprising sulfonate moieties; and (iii) 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):

formula (I):



wherein in formula (I), R_0 represents a hydrogen atom or CH_3 group, R represents a CH_2 group, CH_2CH_2 group or single bond, X represents a number 0-5 provided X represents a number 1-5 when R is a single bond, and R_1 is a hydrogen atom or C_1 to C_{20} organic group;

formula (II)



in formula (II), R_0 represents a hydrogen atom or CH_3 group, R represents a CH_2 group, CH_2CH_2 group or single bond, X represents a number 0-5, and R_1 is a hydrogen atom or C_1 to C_{20} organic group.

[0076] Polyethylene glycol polymer: Suitable polyethylene glycol polymers include random graft co-polymers comprising: (i) hydrophilic backbone comprising polyethylene glycol; and (ii) hydrophobic side chain(s) selected from the group consisting of: C_4-C_{25} alkyl group, polypropylene, polybutylene, vinyl ester of a saturated C_1-C_6 mono-carboxylic acid, C_1-C_6 alkyl ester of acrylic or methacrylic acid, and mixtures thereof. 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 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 polyethylene glycol polymer is Sokalan HP22.

[0077] Polyester soil release polymers: Suitable polyester soil release polymers have a structure as defined by one of the following structures (I), (II) or (III):

(I) $-[(OCHR^1\text{-}CHR^2)_a\text{-}O\text{-}OC\text{-}Ar\text{-}CO\text{-}]_d$

(II) $-[(OCHR^3\text{-}CHR^4)_b\text{-}O\text{-}OC\text{-}sAr\text{-}CO\text{-}]_e$

(III) $-[(OCHR^5\text{-}CHR^6)_c\text{-}OR^7]_f$

wherein:

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 H, Na, Li, K, Mg/2, Ca/2, Al/3, ammonium, mono-, di-, tri-, or tetraalkylammonium wherein the alkyl groups are C_1-C_{18} alkyl or C_2-C_{10} hydroxyalkyl, or any mixture 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. Suitable polyester soil release polymers are terephthalate polymers having the structure of formula (I) or (II) above.

[0078] Suitable polyester soil release polymers include the Repel-o-tex series of polymers such as Repel-o-tex SF2 (Rhodia) and/or the Texcare series of polymers such as Texcare SRA300 (Clariant).

[0079] Other preferred PEI polymers are described in WO2014/114570.

[0080] **Amine polymer:** Suitable amine polymers include polyethylene imine polymers, such as alkoxylated polyalkyleneimines, optionally comprising a polyethylene and/or polypropylene oxide block.

[0081] **Cellulosic polymer:** The composition can comprise cellulosic polymers, such as polymers selected from alkyl cellulose, alkyl alkoxyalkyl cellulose, carboxyalkyl cellulose, alkyl carboxyalkyl, and any combination thereof. Suitable cellulosic polymers are selected from carboxymethyl cellulose, methyl cellulose, methyl hydroxyethyl cellulose, methyl carboxymethyl cellulose, and mixtures thereof. The carboxymethyl cellulose can have a degree of carboxymethyl substitution from 0.5 to 0.9 and a molecular weight from 100,000 Da to 300,000 Da. Another suitable cellulosic polymer is hydrophobically modified carboxymethyl cellulose, such as Finnfix SH-1 (CP Kelco).

[0082] Other suitable cellulosic polymers may have a degree of substitution (DS) of from 0.01 to 0.99 and a degree of blockiness (DB) such that either DS+DB is of at least 1.00 or DB+2DS-DS^2 is at least 1.20. The substituted cellulosic polymer can have a degree of substitution (DS) of at least 0.55. The substituted cellulosic polymer can have a degree of blockiness (DB) of at least 0.35. The substituted cellulosic polymer can have a DS + DB, of from 1.05 to 2.00. A suitable substituted cellulosic polymer is carboxymethylcellulose.

[0083] Another suitable cellulosic polymer is cationically modified hydroxyethyl cellulose.

[0084] **Dye transfer inhibitor polymer:** The laundry detergent compositions may comprise DTI polymers. Suitable DTIs include polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidone polymers, polyvinyloxazolidones and polyvinylimidazoles or mixtures thereof. The DTI polymers discussed above are well known in the art and commercially available, for example PVP-K15 and K30 (Ashland), Sokalan HP165, HP50, HP53, HP59, HP56K, HP56, HP66 (BASF), Chromabond S-400, S403E and S-100 (Ashland), and Polyquart FDI (Cognis).

[0085] **Hexamethylenediamine derivative polymers:** Suitable polymers includehexamethylenediamine derivative polymers, typically having the formula:

$$R_2(CH_3)N^+(CH_2)6N^+(CH_3)R_2.\ 2X^-$$

wherein X- is a suitable counter-ion, for example chloride, and R is a poly(ethylene glycol) chain having an average degree of ethoxylation of from 20 to 30. Optionally, the poly(ethylene glycol) chains may be independently capped with sulphate and/or sulphonate groups, typically with the charge being balanced by reducing the number of X- counter-ions, or (in cases where the average degree of sulphation per molecule is greater than two), introduction of Y^+ counter-ions, for example sodium cations.

[0086] **Builder:** Suitable builders include zeolites, phosphates, citrates, and any combination thereof.

[0087] **Zeolite builder:** The composition may be substantially free of zeolite builder. Substantially free of zeolite builder typically means comprises from 0wt% to 10wt%, zeolite builder, or to 8wt%, or to 6wt%, or to 4wt%, or to 3wt%, or to 2wt%, or even to 1wt% zeolite builder. Substantially free of zeolite builder preferably means "no deliberately added" zeolite builder. Typical zeolite builders include zeolite A, zeolite P, zeolite MAP, zeolite X and zeolite Y.

[0088] **Phosphate builder:** The composition may be substantially free of phosphate builder. Substantially free of phosphate builder typically means comprises from 0wt% to 10wt% phosphate builder, or to 8wt%, or to 6wt%, or to 4wt%, or to 3wt%, or to 2wt%, or even to 1wt% phosphate builder. Substantially free of zeolite builder preferably preferably means "no deliberately added" phosphate builder. A typical phosphate builder is sodium tri-polyphosphate (STPP).

[0089] **Citrate:** A suitable citrate is sodium citrate. However, citric acid may also be incorporated into the composition, which can form citrate in the wash liquor.

[0090] **Buffer and alkalinity source:** Suitable buffers and alkalinity sources include carbonate salts and/or silicate salts and/or double salts such as burkeitte.

[0091] **Carbonate salt:** A suitable carbonate salt is sodium carbonate and/or sodium bicarbonate. The composition

may comprise bicarbonate salt. It may be suitable for the composition to comprise low levels of carbonate salt, for example, it may be suitable for the composition to comprise from 0wt% to 10wt% carbonate salt, or to 8wt%, or to 6wt%, or to 4wt%, or to 3wt%, or to 2wt%, or even to 1wt% carbonate salt. The composition may even be substantially free of carbonate salt; substantially free means "no deliberately added".

[0092] The carbonate salt may have a weight average mean particle size of from 100 to 500 micrometers. Alternatively, the carbonate salt may have a weight average mean particle size of from 10 to 25 micrometers.

[0093] **Silicate salt:** The composition may comprise from 0wt% to 20wt% silicate salt, or to 15wt%, or to 10wt%, or to 5wt%, or to 4wt%, or even to 2wt%, and may comprise from above 0wt%, or from 0.5wt%, or even from 1wt% silicate salt. The silicate can be crystalline or amorphous. Suitable crystalline silicates include crystalline layered silicate, such as SKS-6. Other suitable silicates include 1.6R silicate and/or 2.0R silicate. A suitable silicate salt is sodium silicate. Another suitable silicate salt is sodium metasilicate.

[0094] **Filler:** The composition may comprise from 0wt% to 70% filler. Suitable fillers include sulphate salts and/or bio-filler materials.

[0095] **Sulphate salt:** A suitable sulphate salt is sodium sulphate. The sulphate salt may have a weight average mean particle size of from 100 to 500 micrometers, alternatively, the sulphate salt may have a weight average mean particle size of from 10 to 45 micrometers.

[0096] **Bio-filler material:** A suitable bio-filler material is alkali and/or bleach treated agricultural waste.

[0097] **Bleach:** The composition may comprise bleach. Alternatively, the composition may be substantially free of bleach; substantially free means "no deliberately added". Suitable bleach includes bleach activators, sources of available oxygen, pre-formed peracids, bleach catalysts, reducing bleach, and any combination thereof. If present, the bleach, or any component thereof, for example the pre-formed peracid, may be coated, such as encapsulated, or clathrated, such as with urea or cyclodextrin.

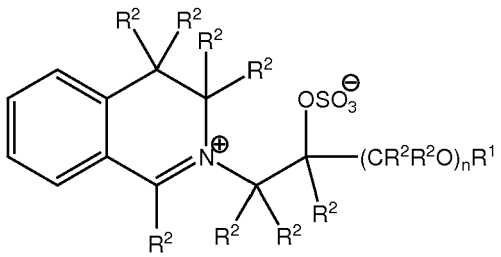
[0098] **Bleach activator:** Suitable bleach activators include: tetraacetylethylenediamine (TAED); oxybenzene sulphonates such as nonanoyl oxybenzene sulphonate (NOBS), caprylamidononanoyl oxybenzene sulphonate (NACA-OBS), 3,5,5-trimethyl hexanoyloxybenzene sulphonate (Iso-NOBS), dodecyl oxybenzene sulphonate (LOBS), and any mixture thereof; caprolactams; pentaacetate glucose (PAG); nitrile quaternary ammonium; imide bleach activators, such as N-nonanoyl-N-methyl acetamide; and any mixture thereof.

[0099] **Source of available oxygen:** A suitable source of available oxygen (AvOx) is a source of hydrogen peroxide, such as percarbonate salts and/or perborate salts, such as sodium percarbonate. The source of peroxygen may be at least partially coated, or even completely coated, by a coating ingredient such as a carbonate salt, a sulphate salt, a silicate salt, borosilicate, or any mixture thereof, including mixed salts thereof. Suitable percarbonate salts can be prepared by a fluid bed process or by a crystallization process. Suitable perborate salts include sodium perborate mono-hydrate (PB1), sodium perborate tetra-hydrate (PB4), and anhydrous sodium perborate which is also known as fizzing sodium perborate. Other suitable sources of AvOx include persulphate, such as oxone. Another suitable source of AvOx is hydrogen peroxide.

[0100] **Pre-formed peracid:** A suitable pre-formed peracid is N,N-pthaloylamino peroxycaproic acid (PAP).

[0101] **Bleach catalyst:** Suitable bleach catalysts include oxaziridinium-based bleach catalysts, transition metal bleach catalysts and bleaching enzymes.

[0102] **Oxaziridinium-based bleach catalyst:** A suitable oxaziridinium-based bleach catalyst has the formula:



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

[0103] **Transition metal bleach catalyst:** The composition may include transition metal bleach catalyst, typically

comprising copper, iron, titanium, ruthenium, tungsten, molybdenum, and/or manganese cations. Suitable transition metal bleach catalysts are manganese-based transition metal bleach catalysts.

[0104] **Reducing bleach:** The composition may comprise a reducing bleach. However, the composition may be substantially free of reducing bleach; substantially free means "no deliberately added". Suitable reducing bleach include sodium sulphite and/or thiourea dioxide (TDO).

[0105] **Co-bleach particle:** The composition may comprise a co-bleach particle. Typically, the co-bleach particle comprises a bleach activator and a source of peroxide. It may be highly suitable for a large amount of bleach activator relative to the source of hydrogen peroxide to be present in the co-bleach particle. The weight ratio of bleach activator to source of hydrogen peroxide present in the co-bleach particle can be at least 0.3:1, or at least 0.6:1, or at least 0.7:1, or at least 0.8:1, or at least 0.9:1, or at least 1.0:1.0, or even at least 1.2:1 or higher.

[0106] The co-bleach particle can comprise: (i) bleach activator, such as TAED; and (ii) a source of hydrogen peroxide, such as sodium percarbonate. The bleach activator may at least partially, or even completely, enclose the source of hydrogen peroxide.

[0107] The co-bleach particle may comprise a binder. Suitable binders are carboxylate polymers such as polyacrylate polymers, and/or surfactants including non-ionic detersive surfactants and/or anionic detersive surfactants such as linear C_{11}-C_{13} alkyl benzene sulphonate.

[0108] The co-bleach particle may comprise bleach catalyst, such as an oxaziridium-based bleach catalyst.

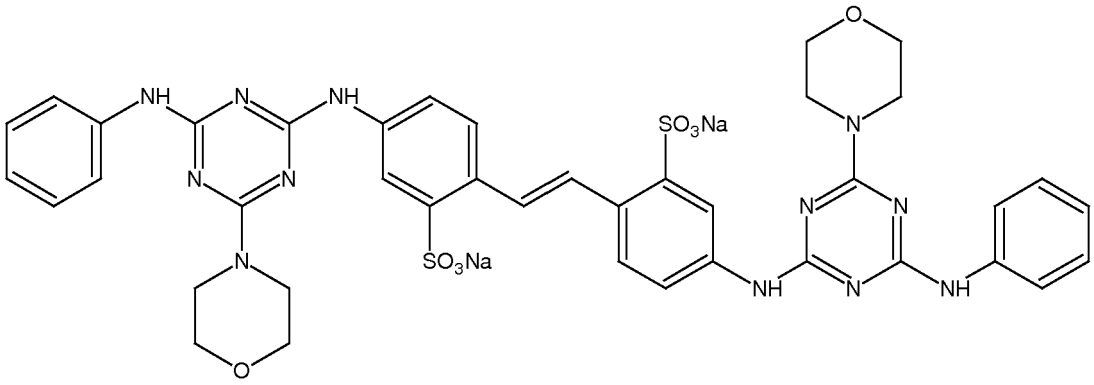
[0109] **Chelant:** Suitable chelants are selected from: diethylene triamine pentaacetate, diethylene triamine penta(methyl phosphonic acid), ethylene diamine-N'N'-disuccinic acid, ethylene diamine tetraacetate, ethylene diamine tetra(methylene phosphonic acid), hydroxyethane di(methylene phosphonic acid), and any combination thereof. A suitable chelant is ethylene diamine-N'N'-disuccinic acid (EDDS) and/or hydroxyethane diphosphonic acid (HEDP). The laundry detergent composition may comprise ethylene diamine-N'N'- disuccinic acid or salt thereof. The ethylene diamine-N'N'-disuccinic acid may be in S,S enantiomeric form. The composition may comprise 4,5-dihydroxy-m-benzenedisulfonic acid disodium salt. Suitable chelants may also be calcium crystal growth inhibitors.

[0110] **Calcium carbonate crystal growth inhibitor:** The composition may comprise a calcium carbonate crystal growth inhibitor, such as one selected from the group consisting of: 1-hydroxyethanediphosphonic acid (HEDP) and salts thereof; N,N-dicarboxymethyl-2-aminopentane-1,5-dioic acid and salts thereof; 2-phosphonobutane-1,2,4-tricarboxylic acid and salts thereof; and any combination thereof.

[0111] **Photobleach:** Suitable photobleaches are zinc and/or aluminium sulphonated phthalocyanines.

[0112] **Brightener:** The laundry detergent compositions may comprise fluorescent brightener. Preferred classes of fluorescent brightener are: Di-styryl biphenyl compounds, e.g. Tinopal™ CBS-X, Di-amino stilbene di-sulfonic acid compounds, e.g. Tinopal™ DMS pure Xtra and Blankophor™ HRH, and Pyrazoline compounds, e.g. Blankophor™ SN. Preferred fluorescers are: sodium 2 (4-styryl-3-sulfophenyl)-2H-napthol[1,2-d]triazole, disodium 4,4'-bis{[(4-anilino-6-(N methyl-N-2 hydroxyethyl)amino 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.

[0113] A particularly preferred fluorescent brightener is C.I. Fluorescent Brightener 260 having the following structure. For solid detergent compositions, this brightener may be used in its beta or alpha crystalline forms, or a mixture of these forms.



[0114] Enzyme: Suitable enzymes include proteases, amylases, cellulases, lipases, xylogucanases, pectate lyases, mannanases, bleaching enzymes, cutinases, and mixtures thereof.

[0115] For the enzymes, accession numbers and IDs shown in parentheses refer to the entry numbers in the databases Genbank, EMBL and/or Swiss-Prot. For any mutations, standard 1-letter amino acid codes are used with a * representing a deletion. Accession numbers prefixed with DSM refer to micro-organisms deposited at Deutsche Sammlung von

Mikroorganismen und Zellkulturen GmbH, Mascheroder Weg 1b, 38124 Brunswick (DSMZ).

[0116] **Protease.** The composition may comprise a protease. Suitable proteases include metalloproteases and/or serine proteases, including neutral or alkaline microbial serine proteases, such as subtilisins (EC 3.4.21.62). Suitable proteases include those of animal, vegetable or microbial origin. In one aspect, such suitable protease may be of microbial origin. The suitable proteases include chemically or genetically modified mutants of the aforementioned suitable proteases. In one aspect, the suitable protease may be a serine protease, such as an alkaline microbial protease or/and a trypsin-type protease. Examples of suitable neutral or alkaline proteases include:

(a) subtilisins (EC 3.4.21.62), including those derived from *Bacillus,* such as *Bacillus lentus, Bacillus alkalophilus* (P27963, ELYA_BACAO), *Bacillus subtilis, Bacillus amyloliquefaciens* (P00782, SUBT_BACAM), *Bacillus pumilus (P07518) and Bacillus gibsonii* (DSM14391).

(b) trypsin-type or chymotrypsin-type proteases, such as trypsin (e.g. of porcine or bovine origin), including the Fusarium protease and the chymotrypsin proteases derived from *Cellumonas* (A2RQE2).

(c) metalloproteases, including those derived from *Bacillus amyloliquefaciens* (P06832, NPRE_BACAM).

[0117] Suitable proteases include those derived from *Bacillus gibsonii* or *Bacillus Lentus* such as subtilisin 309 (P29600) and/or DSM 5483 (P29599).

[0118] 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 (P29599 having the following mutations S99D + S101 R + S103A + V104I + G159S), and variants thereof including 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.

[0119] Other suitable protease enzymes are fungal serine proteases. Suitable enzymes are variants or wild-types of the fungal serine proteases endogenous to *Trichoderma reesei* strain QM9414, *Malbranchea cinnamomea* strain ALK04122, *Fusarium graminearum* strain ALK01726, *Fusarium equiseti* strain CBS 119568 and *Fusarium acuminatum* strain CBS 124084. Examples of commercially available fungal serine proteases are Biotouch ROC and Biotouch Novia, both supplied by AB Enzymes, Darmstadt, Germany.

[0120] **Amylase:** Suitable amylases are alpha-amylases, including those of bacterial or fungal origin. Chemically or genetically modified mutants (variants) are included. A suitable alkaline alpha-amylase is derived from a strain of *Bacillus,* such as *Bacillus licheniformis, Bacillus amyloliquefaciens, Bacillus stearothermophilus, Bacillus subtilis,* or other *Bacillus sp.,* such as *Bacillus sp.* NCIB 12289, NCIB 12512, NCIB 12513, sp 707, DSM 9375, DSM 12368, DSMZ no. 12649, KSM AP1378, KSM K36 or KSM K38. Suitable amylases include:

(a) alpha-amylase derived from *Bacillus licheniformis* (P06278, AMY_BACLI), and variants thereof, especially the variants with substitutions in one or more of the following positions: 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) AA560 amylase (CBU30457, HD066534) and variants thereof, especially the variants with one or more substitutions in the following positions: 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, optionally that also contain the deletions of D183* and G184*.

(c) variants exhibiting at least 90% identity with the wild-type enzyme from *Bacillus SP722* (CBU30453, HD066526), especially variants with deletions in the 183 and 184 positions.

[0121] Suitable commercially available alpha-amylases are Duramyl®, Liquezyme® Termamyl®, Termamyl Ultra®, Natalase®, Supramyl®, Stainzyme®, Stainzyme Plus®, Fungamyl® and BAN® (Novozymes A/S), Bioamylase® and variants thereof (Biocon India Ltd.), Kemzym® AT 9000 (Biozym Ges. m.b.H, Austria), Rapidase®, Purastar®, Optisize HT Plus®, Enzysize®, Powerase® and Purastar Oxam®, Maxamyl® (Genencor International Inc.) and KAM® (KAO, Japan). Suitable amylases are Natalase®, Stainzyme® and Stainzyme Plus®.

[0122] **Cellulase:** The composition may comprise a cellulase. Suitable cellulases include those of bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Suitable cellulases include cellulases from the genera *Bacillus, Pseudomonas, Humicola, Fusarium, Thielavia, Acremonium,* e.g., the fungal cellulases produced from *Humicola insolens, Myceliophthora thermophila* and *Fusarium oxysporum.*

[0123] Commercially available cellulases include Celluzyme®, and Carezyme® (Novozymes A/S), Clazinase®, and

Puradax HA® (Genencor International Inc.), and KAC-500(B)® (Kao Corporation).

[0124] The cellulase can include microbial-derived endoglucanases exhibiting endo-beta-1,4-glucanase activity (E.C. 3.2.1.4), including a bacterial polypeptide endogenous to a member of the genus *Bacillus sp. AA349* and mixtures thereof. Suitable endoglucanases are sold under the tradenames Celluclean® and Whitezyme® (Novozymes A/S, Bagsvaerd, Denmark).

[0125] The composition may comprise a cleaning cellulase belonging to Glycosyl Hydrolase family 45 having a molecular weight of from 17kDa to 30 kDa, for example the endoglucanases sold under the tradename Biotouch® NCD, DCC and DCL (AB Enzymes, Darmstadt, Germany).

[0126] Suitable cellulases may also exhibit xyloglucanase activity, such as Whitezyme®.

[0127] **Lipase.** The composition may comprise a lipase. Suitable lipases include those of bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Examples of useful lipases include lipases from *Humicola* (synonym *Thermomyces),* e.g., from *H. lanuginosa (T. lanuginosus),* or from *H. insolens,* a Pseudomonas lipase, e.g., from *P. alcaligenes* or *P. pseudoalcaligenes, P. cepacia, P. stutzeri, P. fluorescens, Pseudomonas* sp. strain SD 705, *P. wisconsinensis,* a *Bacillus* lipase, e.g., from *B. subtilis, B. stearothermophilus* or *B. pumilus.*

[0128] The lipase may be a "first cycle lipase", optionally a variant of the wild-type lipase from *Thermomyces lanuginosus* comprising T231R and N233R mutations. The wild-type sequence is the 269 amino acids (amino acids 23 - 291) of the Swissprot accession number Swiss-Prot 059952 (derived from *Thermomyces lanuginosus (Humicola lanuginosa)).* Suitable lipases would include those sold under the tradenames Lipex®, Lipolex® and Lipoclean® by Novozymes, Bagsvaerd, Denmark.

[0129] The composition may comprise a variant of *Thermomyces lanuginosa* (059952) lipase having >90% identity with the wild type amino acid and comprising substitution(s) at T231 and/or N233, optionally T231R and/or N233R.

[0130] **Xyloglucanase:** Suitable xyloglucanase enzymes may have enzymatic activity towards both xyloglucan and amorphous cellulose substrates. The enzyme may be a glycosyl hydrolase (GH) selected from GH families 5, 12, 44 or 74. The glycosyl hydrolase selected from GH family 44 is particularly suitable. Suitable glycosyl hydrolases from GH family 44 are the XYG1006 glycosyl hydrolase from *Paenibacillus polyxyma* (ATCC 832) and variants thereof.

[0131] **Pectate lyase:** Suitable pectate lyases are either wild-types or variants of Bacillus-derived pectate lyases (CAF05441, AAU25568) sold under the tradenames Pectawash®, Pectaway® and X-Pect® (from Novozymes A/S, Bagsvaerd, Denmark).

[0132] **Mannanase:** Suitable mannanases are sold under the tradenames Mannaway® (from Novozymes A/S, Bagsvaerd, Denmark), and Purabrite® (Genencor International Inc., Palo Alto, California).

[0133] **Bleaching enzyme:** Suitable bleach enzymes include oxidoreductases, for example oxidases such as glucose, choline or carbohydrate oxidases, oxygenases, catalases, peroxidases, like halo-, chloro-, bromo-, lignin-, glucose- or manganese-peroxidases, dioxygenases or laccases (phenoloxidases, polyphenoloxidases). Suitable commercial products are sold under the Guardzyme® and Denilite® ranges from Novozymes. It may be advantageous for additional organic compounds, especially aromatic compounds, to be incorporated with the bleaching enzyme; these compounds interact with the bleaching enzyme to enhance the activity of the oxidoreductase (enhancer) or to facilitate the electron flow (mediator) between the oxidizing enzyme and the stain typically over strongly different redox potentials.

[0134] Other suitable bleaching enzymes include perhydrolases, which catalyse the formation of peracids from an ester substrate and peroxygen source. Suitable perhydrolases include variants of the Mycobacterium smegmatis perhydrolase, variants of so-called CE-7 perhydrolases, and variants of wild-type subtilisin Carlsberg possessing perhydrolase activity.

[0135] **Cutinase:** Suitable cutinases are defined by E.C. Class 3.1.1.74, optionally displaying at least 90%, or 95%, or most optionally at least 98% identity with a wild-type derived from one of *Fusarium solani, Pseudomonas mendocina* or *Humicola insolens.* Suitable cutinases can be selected from wild-types or variants of cutinases endogenous to strains of *Aspergillus,* in particular *Aspergillus oryzae,* a strain of *Alternaria,* in particular *Alternaria brassiciola,* a strain of *Fusarium,* in particular *Fusarium solani, Fusarium solani pisi, Fusarium oxysporum, Fusarium oxysporum cepa, Fusarium roseum culmorum,* or *Fusarium roseum sambucium,* a strain of *Helminthosporum,* in particular *Helminthosporum sativum,* a strain of *Humicola,* in particular *Humicola insolens,* a strain of *Pseudomonas,* in particular *Pseudomonas mendocina,* or *Pseudomonas putida,* a strain of *Rhizoctonia,* in particular *Rhizoctonia solani,* a strain of *Streptomyces,* in particular *Streptomyces scabies,* a strain of *Coprinopsis,* in particular *Coprinopsis cinerea,* a strain of *Thermobifida,* in particular *Thermobifida fusca,* a strain of *Magnaporthe,* in particular *Magnaporthe grisea,* or a strain of *Ulocladium,* in particular *Ulocladium consortiale.*

[0136] In a preferred embodiment, the cutinase is selected from variants of the *Pseudomonas mendocina* cutinase described in WO 2003/076580 (Genencor), such as the variant with three substitutions at I178M, F180V, and S205G.

[0137] In another preferred embodiment, the cutinase is a wild-type or variant of the six cutinases endogenous to *Coprinopsis cinerea* described in H. Kontkanen et al, App. Environ. Microbiology, 2009, p2148-2157

[0138] In another preferred embodiment, the cutinase is a wild-type or variant of the two cutinases endogenous to *Trichoderma reesei* described in WO2009007510 (VTT).

[0139] In a most preferred embodiment the cutinase is derived from a strain of *Humicola insolens,* in particular the strain *Humicola insolens* DSM 1800. *Humicola insolens* cutinase is described in WO 96/13580 which is hereby incorporated by reference. The cutinase may be a variant, such as one of the variants disclosed in WO 00/34450 and WO 01/92502. Preferred cutinase variants include variants listed in Example 2 of WO 01/92502.

[0140] **Identity.** The relativity between two amino acid sequences is described by the parameter "identity". For purposes of the present invention, the alignment of two amino acid sequences is determined by using the Needle program from the EMBOSS package (http://emboss.org) version 2.8.0. The Needle program implements the global alignment algorithm described in Needleman, S. B. and Wunsch, C. D. (1970) J. Mol. Biol. 48, 443-453. The substitution matrix used is BLOSUM62, gap opening penalty is 10, and gap extension penalty is 0.5.

[0141] **Fabric-softener:** Suitable fabric-softening agents include clay, silicone and/or quaternary ammonium compounds. Suitable clays include montmorillonite clay, hectorite clay and/or laponite clay. A suitable clay is montmorillonite clay. Suitable silicones include amino-silicones and/or polydimethylsiloxane (PDMS). A suitable fabric softener is a particle comprising clay and silicone, such as a particle comprising montmorillonite clay and PDMS.

[0142] **Flocculant:** Suitable flocculants include polyethylene oxide; for example having an average molecular weight of from 300,000 Da to 900,000 Da.

[0143] **Suds suppressor:** Suitable suds suppressors include silicone and/or fatty acid such as stearic acid.

[0144] **Perfume:** Suitable perfumes include perfume microcapsules, polymer assisted perfume delivery systems including Schiff base perfume/polymer complexes, starch-encapsulated perfume accords, perfume-loaded zeolites, blooming perfume accords, and any combination thereof. A suitable perfume microcapsule is melamine formaldehyde based, typically comprising perfume that is encapsulated by a shell comprising melamine formaldehyde. It may be highly suitable for such perfume microcapsules to comprise cationic and/or cationic precursor material in the shell, such as polyvinyl formamide (PVF) and/or cationically modified hydroxyethyl cellulose (catHEC).

[0145] **Aesthetic:** Suitable aesthetic particles include soap rings, lamellar aesthetic particles, geltin beads, carbonate and/or sulphate salt speckles, coloured clay particles, and any combination thereof.

EXAMPLES

Example 1

[0146] The improved soil removal benefit of the method of the present invention was demonstrated in the following experiment.

[0147] A composition was prepared comprising 100ppm alkyl ethoxylated sulphate anionic surfactant, 46ppm polydimethyl siloxane containing suds suppressor and 400ppm sodium bicarbonate. This composition was labeled pre-condition composition 1.

[0148] A second pre-condition composition was prepared comprising the same ingredients as pre-condition composition 1 but also comprising a lipid esterase variant having at least 90% sequence identity to wild-type lipase from *Thermomyces lanuginosus* and having sequence substitutions T231R and N233R. This was added to the wash liquor at a concentration of 0.3ppm (active enzyme protein). This composition was labelled pre-condition composition 2.

[0149] Standard fabric swatches WFK80A cotton (15x15cm swatches) were obtained from WFK Testgewebe GmbH. Also obtained were swatches of cotton sheet and cotton towels supplied by Test Fabrics to be included as clean ballast.

[0150] Sixty swatches of WFK80A fabric were added to the drum of a Miele 1714 washing machine together with the relevant pre-treatment composition and clean ballast consisting of 2.5kg total weight of cotton sheets and towels at a ratio of 50:50. The swatches were then washed in the 'short cotton cycle' (40°C) at 1600rpm and dried on a line. The pre-treatment compositions were prepared such that the 13L wash liquor comprised a ratio of anionic surfactant:fabric of 1:424 (100ppm anionic surfactant present in the wash liquor). Sodium bicarbonate was added to the wash liquor at a concentration of 400ppm, and the suds suppressor (12.4% active) at a concentration of 46ppm. The lipid esterase was added to the wash liquor at a concentration of 0.3ppm.

[0151] The WFK80A fabric from pre-condition compositions 1 and 2 were cut into 5cmx5cm squares, which were each stained with 200 μL of SV13-dyed Bacon Grease (supplied by Warwick Equest, County Durham, United Kingdom, SV13 %, batch SPt001013) and were stored at 32°C/80%rh overnight.

[0152] Some of the stained swatches were first subjected to a stain pre-treatment comprising the detergent composition detailed in Table 1 with or without the addition of lipid esterase. The stain pre-treatment process involves direct contact of the detergent composition with the stain surface, forming a concentrated cleaning composition. The stain surface was covered with 0.4ml detergent using a disposable syringe. Stains were left for five minutes before being added into the 1L Tergotometer pot containing the remaining detergent with or without the addition of lipid esterase that was not used in the pre-treatment step. The swatches that were not subject to the stain pre-treatment step were also added into the 1L Tergotometer pot in the presence of the Western European liquid detergent detailed in Table 1. For all fabrics tested the detergent was dosed at a concentration of 3860ppm with or without the addition of the lipid esterase at concentration

of 0.3ppm . Ballast fabric made up of knitted cotton fabric was also added, with an overall fabric load of 24.8g. Wash conditions in the Tergotometer were 200rpm, wash time 20 minutes at 20°C and rinse time of three minutes. Fabrics were then air dried overnight on metal racks.

Table 1: Detergent Composition	(wt%)
Linear alkylbenzene sulfonate	7.518
Citric acid	3.23
C_{12-18} fatty acid	3.14
Sodium C_{12-14} alkyl ethoxy 3 sulfate	2.609
C_{14-15} alkyl 7-ethoxylate	4.420
C_{12-14} alkyl -7-ethoxylate	0.426
Calcium chloride dehydrate	0.020
A compound having the following general structure: bis($(C_2H_5O)(C_2H_4O)n$)((CH_3)-N^+-C_xH_{2x}-N^+-((CH_3)-bis(($(C_2H_5O)(C_2H_4O)n$), wherein n = from 20 to 30, and x = from 3 to 8, or sulphated or sulphonated variants thereof	1.00
Random graft co-polymer[1]	0.5
Diethylene triamine penta (methylene phosphonic acid)	0.28
Tinopal® TAS-X B36	0.092
Monoethanolamine	0.304
Sodium hydroxide	3.704
Sodium cumene sulphonate	0.930
Sodium formate	0.4
Water, aesthetics, (dyes, perfumes) and minors (enzymes, solvents, structurants)	71.426
[1]Random graft copolymer is a polyvinyl acetate grafted polyethylene oxide copolymer having a polyethylene oxide backbone and multiple polyvinyl acetate side chains. The molecular weight of the polyethylene oxide backbone is about 6000 and the weight ratio of the polyethylene oxide to polyvinyl acetate is about 40 to 60 and no more than 1 grafting point per 50 ethylene oxide units.	

[0153] Lipid esterase was added at a concentration of 0.3ppm (active enzyme protein) to the pre-condition, stain pre-treatment and wash compositions so that the level of lipid esterase remains the same across all compositions.

[0154] Stain removal was quantified using commercially available Digieye software to calculate percentage stain removal from L*a*b* values. The software generates the L value, the a value and the b value, and percentage stain removal was calculated using the following equation; %SR (stain removal) = $100*((\Delta E_b - \Delta E_a)/\Delta E_b)$

$$\Delta E_b = \sqrt{((L_c-L_b)^2 + (a_c-a_b)^2 + b_c-b_b)^2)}$$

$$\Delta E_a = \sqrt{((L_c-L_a)^2 + (a_c-a_a)^2 + b_c-b_a)^2)}$$

Subscript 'b' denotes data for the stain before washing
Subscript 'a' denotes data for the stain after washing
Subscript 'c' denotes data for the unstained fabric

[0155] Thus, L*a*b* values are taken of the unstained fabric, of the stained fabric before washing and of the stained fabric after washing.

[0156] The following combinations were tested and compared;

Table 2

	Pre-Condition Composition	Pre-treatment Composition	Wash Composition
A	1	N/A	Detergent
B	1	N/A	Detergent + lipid esterase
C	1	Detergent	Detergent
D	1	Detergent + lipid esterase	Detergent
E	2	N/A	Detergent
F	2	N/A	Detergent + lipid esterase
G	2	Detergent	Detergent
H	2	Detergent + lipid esterase	Detergent

[0157] Results can be seen in table 3.

Table 3

	%SR	Standard Error
A	34	2.8
B	40	1.6
C	41	2.1
D	49	1.3
E	61	2.6
F	60	1.5
G	63	2.0
H	76	1.3
(Standard error was calculated as SE = SD/$\sqrt{n}$ where SD = standard deviation and n = number of external replicates)		

[0158] The data clearly show that the fabrics treated with pre-condition 2, i.e. detergent with added lipid esterase (E-H in Table 3) showed higher percentage soil removal than those treated with pre-condition 1, i.e. no enzyme present (A-D in Table 3). The addition of a five minute stain pre-treatment step with detergent alone also increased soil removal compared to those without the stain pre-treatment step. However what is surprising is the combination of fabrics treated with pre-condition 2 and the combination of a stain pre-treatment with detergent and lipid esterase (H is Table 3) result in the highest stain removal of all combinations tested.

Examples 2-13;

[0159] The following examples are of laundry detergent compositions suitable for use in step (iii);

Examples 2-7 Heavy Duty Liquid laundry detergent compositions.

[0160] Heavy duty liquid laundry detergent compositions designed for front-loading washing machines may be used for direct contact with the surface to be treated, forming a concentrated cleaning composition.

	2 (wt%)	3 (wt%)	4 (wt%)	5 (wt%)	6 (wt%)	7 (wt%)
AES C_{12-15} alkyl ethoxy (1.8) sulfate	11	10	4	6.32	0	0
AE3S	0	0	0	0	2.4	0
Linear alkyl benzene sulfonate	1.4	4	8	3.3	5	8
HSAS	3	5.1	3	0	0	0
Sodium formate	1.6	0.09	1.2	0.04	1.6	1.2
Sodium hydroxide	2.3	3.8	1.7	1.9	1.7	2.5
Monoethanolamine	1.4	1.49	1.0	0.7	0	0
Diethylene glycol	5.5	0.0	4.1	0.0	0	0
AE9	0.4	0.6	0.3	0.3	0	0
AE7	0	0	0	0	2.4	6
Chelant	0.15	0.15	0.11	0.07	0.5	0.11
Citric acid	2.5	3.96	1.88	1.98	0.9	2.5
C_{12-14} dimethyl amine oxide	0.3	0.73	0.23	0.37	0	0
C_{12-18} fatty ccid	0.8	1.9	0.6	0.99	1.2	0
4-formyl-phenylboronic acid	0	0	0	0	0.05	0.02
Borax	1.43	1.5	1.1	0.75	0	1.07
Ethanol	1.54	1.77	1.15	0.89	0	3
Ethoxylated (EO_{15}) tetraethylene pentamine	0.3	0.33	0.23	0.17	0.0	0.0
Ethoxylated hexamethylene diamine	0.8	0.81	0.6	0.4	1	1
1,2-Propanediol	0	6.6	0	3.3	0.5	2
Random graft co-polymer[1]	0.5	0.3	0	0.6	0.2	0.1
Bacterial protease (54.5 mg active/g)	0.8	0.6	0.7	0.9	0.7	0.6
Mannaway® (25 mg active/g)	0.07	0.05	0.045	0.06	0.04	0.045
Stainzyme® (15 mg active/g)	0.3	0.2	0.3	0.1	0.2	0.4
Natalase® (29 mg active/g)	0	0.2	0.1	0.15	0.07	0
Lipex® (18 mg active/g)	0.4	0.2	0.3	0.1	0.2	0

(continued)

	2 (wt%)	3 (wt%)	4 (wt%)	5 (wt%)	6 (wt%)	7 (wt%)
Whitezyme® (20 mg active/g)	0.2	0.08	0.1	0	0.01	0.05
Biotouch® ROC (20mg active/g)	0.2	0.1	0.2	0.2	0.1	0.1
A compound having the following general structure: $bis((C_2H_5O)(C_2H_4O)_n)(CH_3)\text{-}N^+\text{-}C_xH_{2x}\text{-}N^+\text{-}(CH_3)\text{-}bis((C_2H_5O)(C_2H_4O)n)$, wherein n = from 20 to 30, and x = from 3 to 8, or sulphated or sulphonated variants thereof	1.0	0.8	1.8	2	0	1.3
Liquitint® Violet CT (active)	0.006	0.002	0	0	0	0.002
S-ACMC	0	0	0.01	0.05	0.01	0.02
Water, perfume, dyes & other components	Balance					
[1]Random graft copolymer is a polyvinyl acetate grafted polyethylene oxide copolymer having a polyethylene oxide backbone and multiple polyvinyl acetate side chains. The molecular weight of the polyethylene oxide backbone is about 6000 and the weight ratio of the polyethylene oxide to polyvinyl acetate is about 40 to 60 and no more than 1 grafting point per 50 ethylene oxide units. Remark: all enzyme levels expressed as % enzyme raw material						

[0161] Any of the above compositions is used to launder fabrics in the third step at a concentration of 3000 to 10000 ppm in water, 20-90°C, and a 5:1 water:cloth ratio. The typical pH is about 8. The fabrics are then dried. In one aspect, the fabrics are actively dried using a dryer. In one aspect, the fabrics are actively dried using an iron. In another aspect, the fabrics are merely allowed to dry on a line wherein they are exposed to air and optionally sunlight.

Examples 8-13

[0162] These compositions may be enclosed in a polyvinyl alcohol pouch.

	8 (wt%)	9 (wt%)	10 (wt%)	11 (wt%)	12 (wt%)	13 (wt%)
AE3S	5	8.3	10.1	11.3	13.9	16.7
Linear alkyl benzene sulfonate	21	18	15.5	12	11.3	8.41
Sodium hydroxide	0.1	0.08	0.09	0.07	0.05	0.08
Monoethanolamine	6.9	7.5	5.9	7.3	8	7.6
Diethylene glycol	6.2	5.4	3.9	7.1	4.8	3.2
AE9	9.3	11.2	13	14.1	0	0
AE7	0	0	0	0	8.7	9.9
Chelant	0.1	0.15	0.06	0.05	0	0.2
Citric Acid	0.55	0.7	0.61	0.32	0.46	0
C_{12-14} dimethyl Amine Oxide	0	0	0	0.29	0.4	0.37
C_{12-18} Fatty Acid	12.7	10.8	11.1	10.3	12.5	13.3
Ethoxylated (EO_{15}) tetraethylene pentamine	0	0.2	0.13	0.4	0	0.33
Ethoxylated hexamethylene diamine	0.8	0.73	0	0.48	0.62	0.55
1,2-Propanediol	16	17.4	14.8	18.9	15.3	16.4
Bacterial protease (40.6 mg active/g)	1.5	1.4	1.0	0.9	1.2	0.6
Mannaway® (25 mg active/g)	0.1	0.08	0	0.02	0.04	0.05
Stainzyme® (15 mg active/g)	0.08	0.1	0.07	0	0.1	0
Natalase® (29 mg active/g)	0	0.1	0.2	0.12	0	0.18
Lipex® (18 mg active/g)	0.08	0.2	0.1	0.15	0.03	0.06
Whitezyme® (20 mg active/g)	0.2	0.08	0.1	0	0.01	0.05
Biotouch® ROC (20mg active/g)	0.05	0.2	0.1	0	0.08	0.15
A compound having the following general structure: $bis((C_2H_5O)(C_2H_4O)n)(CH_3)\text{-}N^+\text{-}C_XH_{2X}\text{-}N^+\text{-}(CH_3)\text{-}bis((C_2H_5O)(C_2H_4O)n)$, wherein n = from 20 to 30, and x = from 3 to 8, or sulphated or sulphonated variants thereof	1.0	0.8	1.8	2	0	1.3
Water*, perfume, dyes & other components	Balance to 100%					
* Based on total cleaning and/or treatment composition weight, a total of no more than 9% water						

Raw Materials and Notes For Composition Examples 2-20

[0163]

Linear alkylbenzenesulfonate having an average aliphatic carbon chain length C_{11}-C_{12} supplied by Stepan, Northfield, Illinois, USA

C_{12-14} Dimethylhydroxyethyl ammonium chloride, supplied by Clariant GmbH, Sulzbach, Germany

AE3S is C_{12-15} alkyl ethoxy (3) sulfate supplied by Stepan, Northfield, Illinois, USA

AE7 is C_{12-15} alcohol ethoxylate, with an average degree of ethoxylation of 7, supplied by Huntsman, Salt Lake City, Utah, USA

AE9 is C_{12-13} alcohol ethoxylate, with an average degree of ethoxylation of 9, supplied by Huntsman, Salt Lake City, Utah, USA

HSAS is a mid-branched primary alkyl sulfate with carbon chain length of about 16-17

Suitable chelants are, for example, diethylenetetraamine pentaacetic acid (DTPA) supplied by Dow Chemical, Midland, Michigan, USA or Hydroxyethane di phosphonate (HEDP) supplied by Solutia, St Louis, Missouri, USA Bagsvaerd, Denmark

Natalase®, Stainzyme®, Lipex®, Mannaway® and Whitezyme® are all products of Novozymes, Bagsvaerd, Denmark.

Biotouch® ROC is a product of AB Enzymes, Darmstadt, Germany.

Bacterial protease (examples 8-13) described in US 6,312,936 B 1 supplied by Genencor International, Palo Alto, California, USA

Bacterial protease (examples 14-20) described in US 4,760,025 is supplied by Genencor International, Palo Alto, California, USA

Fluorescent Brightener 1 is Tinopal® AMS, Fluorescent Brightener 2 is Tinopal® CBS-X, Sulphonated zinc phthalocyanine and Direct Violet 9 is Pergasol® Violet BN-Z all supplied by Ciba Specialty Chemicals, Basel, Switzerland

S-ACMC is carboxymethylcellulose conjugated with C.I. Reactive Blue 19, sold by Megazyme, Wicklow, Ireland under the product name AZO-CM-CELLULOSE, product code S-ACMC.

Soil release agent is Repel-o-tex® PF, supplied by Rhodia, Paris, France

Hydroxyethane di phosphonate (HEDP) is supplied by Dow Chemical, Midland, Michigan, USA

Suds suppressor agglomerate is supplied by Dow Corning, Midland, Michigan, USA

HSAS is mid-branched alkyl sulfate as disclosed in US 6,020,303 and US 6,060,443

C_{12-14} dimethyl Amine Oxide is supplied by Procter & Gamble Chemicals, Cincinnati, Ohio, USA

Liquitint® Violet CT is supplied by Milliken, Spartanburg, South Carolina, USA.

[0164] 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 s 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."

[0165] Every document cited herein, including any cross referenced or related patent or application, is hereby incorporated herein by reference in its entirety unless expressly excluded or otherwise limited. The citation of any document

is not an admission that it is prior art with respect to any invention disclosed or claimed herein or that it alone, or in any combination with any other reference or references, teaches, suggests or discloses any such invention. Further, to the extent that any meaning or definition of a term in this document conflicts with any meaning or definition of the same term in a document incorporated by reference, the meaning or definition assigned to that term in this document shall govern.

[0166] While particular embodiments of the present invention have been illustrated and described, it would be obvious to those skilled in the art that various other changes and modifications can be made without departing from the spirit and scope of the invention. It is therefore intended to cover in the appended claims all such changes and modifications that are within the scope of this invention.

Claims

1. A method of laundering a fabric comprising the steps of:

(i) contacting the fabric with a lipid esterase selected from class E.C. 3.1.1.3, class E.C. 3.1.1.1 or a combination thereof;
(ii) contacting the fabric from step (i) with a soil;
(iii) contacting the fabric from step (ii) with a surfactant composition, comprising from 5 to 100 wt% detersive surfactant and optionally additionally comprising a lipid esterase; and
(iv) contacting the fabric from step (iii) with an aqueous wash liquor comprising a detergent composition.

2. A method according to claim 1 wherein the fabric comprises cotton.

3. A method according to claim 1 or claim 2 wherein the laundry detergent composition comprises at least 10 wt% surfactant, or at least 15 wt% surfactant.

4. A method according to any preceding claim wherein the laundry detergent composition comprises a surfactant composition comprising an anionic surfactant, a non-ionic surfactant and optionally additionally a zwitterionic surfactant.

5. A method according to any preceding claim wherein in step (i) the fabric is contacted with a lipid esterase the lipid esterase being present at a concentration of between 30 and 2000 ng enzyme/g fabric, preferably between 50 and 1700 ng enzyme/g fabric, more preferably between 80 and 1600 ng enzyme/g fabric.

6. A method according to any preceding claim wherein the laundry detergent composition in step (iii) comprises a lipid esterase, wherein the lipid esterase is selected from class E.C. 3.1.1.3, class E.C. 3.1.1.1, or a combination thereof.

7. A method according to any preceding claim wherein the aqueous wash liquor in step (iv) comprises a lipid esterase.

8. A method according to any preceding claims wherein the lipid esterase in step (i) is a variant having at least 90% sequence identity to wild-type lipase from *Thermomyces lanuginosus* and having sequence substitutions T231R and N233R.

9. A method according to any preceding claims wherein the ratio of detersive surfactant to fabric on a weight to weight basis in step (iv) is from 1:150 to 1:500.

10. A method according to any preceding claim, wherein the surfactant comprises an anionic detersive surfactant, preferably a linear alkyl benzene sulfonate, alkoxylated anionic surfactant, or a combination thereof.

11. A method according to any preceding claim, wherein the detersive surfactant comprises linear alkylbenzene sulfonate and a co-surfactant, wherein, the co-surfactant is selected from a non-ionic surfactant, an alkoxylated anionic surfactant, or a combination thereof.

12. A method according to any preceding claims, wherein in step (iii) the composition is contacted with the fabric and in step (iv) the aqueous liquor is contacted with the fabric at a temperature of between 5°C and 50°C, preferably between 10°C and 30°C.

13. A method according to any preceding claims, wherein the aqueous wash liquor comprises a hueing agent, a polymer

or a combination thereof.

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EUROPEAN SEARCH REPORT

Application Number
EP 14 18 1485

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A	GB 1 442 418 A (PROCTER & GAMBLE) 14 July 1976 (1976-07-14) * claims; examples *	1-13	
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	2 March 2015	Grittern, Albert

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