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(54) Title: LAUNDRY DETERGENT COMPOSITION

(57) Abstract: The present invention provides an alkoxyated polyethylene imine polymer and surfactant formulation for use in domestic laundry.



WO 2017/174251 A1

LAUNDRY DETERGENT COMPOSITION

Field of the Invention

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The present invention provides an alkoxyated polyethylene imine polymer and surfactant formulation for use in domestic laundry.

Background of the Invention

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Domestic aqueous Laundry liquid detergent formulation containing Linear Alkyl benzene sulfonate anionic surfactant with high levels of an ethoxylated alcohol non-ionic surfactant are ubiquitous. To enhance cleaning performance alkoxyated polyethylene imine polymers, preferably in combination with polyethylene terephthalate soil removal polymers are added. The addition of these polymers greatly reduces the viscosity of the formulation. Effective methods to increase the viscosity of the formulation are required, which preferably enhance the cleaning performance.

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WO2013/087286 (Unilever) discloses liquids formulations containing alkyl ether carboxylic acids, betaines, anionic surfactant, non-ionic surfactant for providing softening benefits.

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WO2014/060235 (Unilever) discloses a laundry detergent composition comprising (a) nonionic surfactant, (b) anionic surfactant, (c) alkyl ether carboxylic acid or carboxylate salt thereof, and, (d) a polyglucosamine or a copolymer of glucosamine and N-acetylglucosamine; and to its use to soften fabrics.

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Summary of the Invention

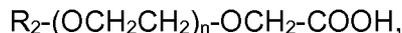
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We have found that addition of alkyl ether carboxylic acid anionic surfactant increases the viscosity of the formulation.

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In one aspect the present invention provides an aqueous liquid laundry detergent composition comprising:

- (i) from 2 to 12 wt%, preferably from 4 to 8 wt%, of a linear alkyl benzene anionic sulfonate surfactant;
- (ii) from 0.5 to 8 wt%, preferably 2 to 4 wt%, of an ethoxylated alcohol non-ionic surfactant, preferably selected from: C10 to C16 primary and secondary aliphatic alcohols ethoxylated with an average of from 6 to 10 moles of ethylene oxide per mole of alcohol, most preferably a C12 to C15 primary aliphatic alcohol with 7 to 9 moles of ethylene oxide per mole of alcohol, preferably the weight fraction of the ethoxylated alcohol non-ionic surfactant/the linear alkyl benzene anionic sulfonate surfactant is from 0.4 to 1.6, more preferably 0.5 to 1.0;
- (iii) from 1 to 8 wt%, preferably 2 to 5 wt%, of an alkoxyated polyethylene imine, preferably ethoxylated polyethylene imine;
- (iv) from 1 to 10 wt%, preferably 2 to 6 wt%, most preferably 3 to 5 wt%, of an alkyl ether carboxylic acid anionic surfactant of the following structure:



wherein:

- R_2 is selected from saturated and mono-unsaturated C10 to C26 linear or branched alkyl chains, preferably a C12 to C20 linear alkyl chains, most preferably a C16 to C18 linear alkyl chain, and wherein n is selected from: 2 to 20, preferably 7 to 13, more preferably 8 to 12, most preferably 9.5 to 10.5;
- (v) from 0 to 4wt%, preferably 0.1 to 3 wt%, more preferably 0.5 to 1.5 wt% of a terephthalate polyester soil release polymer;
- (vi) from 0.0 to 6 wt%, preferably 2 to 5 wt%, of an alkyl ether sulphate with a mole average of 1 to 4.5 moles, preferably 2 to 4, of ethoxylation per surfactant molecule, wherein the weight fraction of alkyl ether sulphate/non-ionic surfactant is less than 1, preferably less than 0.4.

In another aspect the present invention provides a domestic method of treating a textile, the method comprising the steps of:

5 (i) treating a textile with from 1 g/L of the aqueous solution of the laundry detergent composition; and,

(ii) allowing said aqueous laundry detergent solution to remain in contact with the textile for 10 minutes to 2 days then rinsing and drying the textile.

10 In the method aspects of the present invention the surfactant used is preferably as preferred for the composition aspects of the present invention.

Domestic methods are preferably conducted in a domestic washing machine or by hand washing. The temperature of the wash is preferably from 285 to 333K. The main wash time
15 is preferably 10 to 60 minutes.

The textile is preferably an item of clothing, bedding or table cloth. Preferred items of clothing are cotton containing shirts, trousers, underwear and jumpers.

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Detailed Description of the Invention

Linear alkyl benzene sulfonate

Weights of Linear alkyl benzene sulfonate are calculated as the protonated form. The linear
25 alkyl benzene sulfonate has an alkyl chain length of C8 to C15, preferably C12 to C14.

Linear alkyl benzene sulphonate (LAS) may be obtained, by sulphonating commercially available linear alkyl benzene (LAB); suitable LAB includes low 2-phenyl LAB, such as those supplied by Sasol under the tradename Isochem® or those supplied by Petresa under the
30 tradename Petrelab®, other suitable LAB include high 2-phenyl LAB, such as those supplied by Sasol under the tradename Hyblene®. Another suitable route 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.

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Non-ionic surfactant

The aqueous liquid laundry detergent comprises an ethoxylated alcohol non-ionic surfactant, preferably selected from: C10-C15 primary and secondary aliphatic alcohols ethoxylated with an average of from 6 to 10 moles of ethylene oxide per mole of alcohol, most preferably a C12-C15 primary aliphatic alcohol with 7 to 9 moles of ethylene oxide per mole of alcohol, where in the weight fraction of ethoxylated alcohol non-ionic surfactant/ linear alkyl benzene anionic sulfonate surfactant is from 0.4 to 1.6, preferably 0.5 to 1.0, most preferably 0.6 to 0.9

Alkyl ether carboxylic acid

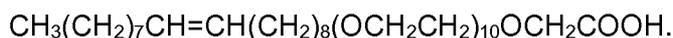
Weights of alkyl ether carboxylic acid are calculated as the protonated form, $R_2-(OCH_2CH_2)_n-OCH_2COOH$. These may be used as salt version for example sodium salt, or amine salt.

The alkyl chain may be linear or branched, preferably it is linear.

The alkyl chain may be aliphatic or contain one cis or trans double bond.

The alkyl chain is preferably selected from: $CH_3(CH_2)_{11}$, $CH_3(CH_2)_{15}$, $CH_3(CH_2)_{17}$, and $CH_3(CH_2)_7CH=CH(CH_2)_8$.

The alkyl ether carboxylic acid is most preferably of the structure:



Alkyl ether carboxylic acid are available from Kao (Akypo®), Huntsman (Empicol®) and Clariant (Emulsogen®). The sodium salt of the alkyl ether carboxylate may be used.

Alkoxyate Polyethylene Imine

The alkoxyated polyethylene imine comprises a polyethyleneimine backbone wherein the modification of the polyethyleneimine backbone is intended to leave the polymer without quaternisation. Such materials may be represented as $PEI(X)YAO$ where X represents the molecular weight of the unmodified PEI and Y represents the average moles of alkoxylation (AO) per available NH in the unsubstituted polyethyleneimine backbone. Y is preferably from 7 to 40 more preferably it is in the range of 16 to 26, most preferably 18 to 22. X is selected

to be from 300 to about 10000 weight average molecular weight and is preferably from 500 to 800.

The alkoxylation is preferably selected from ethoxylation or propoxylation, or a combination of the two, Ethoxylation is most preferred. The alkoxy chains may be capped with groups selected from: H; CH₃; SO₃⁻; CH₂COO⁻; PO₃²⁻; C₂H₅; n-propyl, i-propyl; n-butyl; t-butyl; and, sulfosuccinate, most preferably H.

Most preferably the alkoxyated PEI is PEI(600)20EO.

Further examples are PEI(600)10EO7PO; PEI(1600)19EO; and, PEI80024EO16PO.

To enhance performance of the a co-polymer obtainable by the polymerisation of an alkene bearing a substituent sulfonate group with an alkene bearing a polyoxyalkylene chain and an alkene bearing a carboxy substituents in a weight ratio of from 5:1 to 1:5 with the alkoxyated polyethylenimine may be added. Preferably the co-polymer is obtainable by polymerisation of 5-15wt% 3-allyloxy-2-hydroxypropane sulfonate with 30- to 5wt% of 3-methylbut-3-en-1-ol which has been reacted with 20-40 moles of ethylene oxide; and 25-55% acrylic acid or salts thereof. Such polymers are described in WO2016/045518 (Nippon Shokubai).

Terephthalate Polyester Soil Release Polymer

Terephthalate Polyester Soil Release Polymer comprise polymers of aromatic dicarboxylic acids and alkylene glycols (including polymers containing polyalkylene glycols), as described in WO2009/153184, EP2692842 and WO2014/019903.

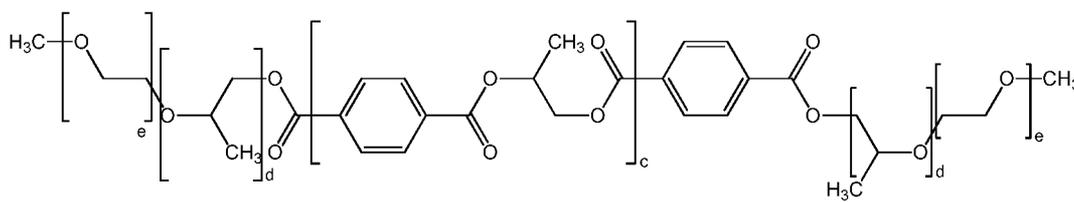
Examples of Terephthalate Polyester Soil Release Polymer are the REPEL-O-TEX® line of polymers supplied by Rhodia, including REPEL-O-TEX® SRP6 and REPEL-O-TEX® SF-2. Other suitable soil release polymers include TexCare® polymers, including TexCare® SRA-100, TexCare® SRA-300, TexCare® SRN-100, TexCare® SRN-170, TexCare® SRN-240, TexCare® SRN-300, and TexCare® SRN-325, all supplied by Clariant.

Preferred structure are $-(Z)_a-O-OC-Ar-CO-]_b$ and $(Z)_a-O-OC-[Ar-CO-O-C_3H_6-O-OC]_b-Ar-CO-O-(Z)_a$, where Ar is selected from 1,4 substituted phenylene and 1,3 substituted phenylene substituted in the 5 position with a sulphonates (SO₃⁻) group; Z is selected from

ethoxy;propoxy; and mixtures of ethoxy and propoxy; a is from 5 to 100 and b from 2 to 40. C₃H₆ is i-propyl.

The alkoxy chains are capped with groups selected from H; CH₃; SO₃⁻; CH₂COO⁻; PO₃²⁻; C₂H₅; n-propyl, i-propyl; n-butyl; t-butyl; and, sulfosuccinate.

Most preferably the Terephthalate Polyester Soil Release Polymer is:



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wherein c is from 4 to 9; d is from 1 to 3; e is from 40 to 50.

Alkyl ether sulfate

Weights of alkyl ether sulfate are calculated as the protonated form, R₁-(OCH₂CH₂)_m-OSO₃H. Preferably R₁ is C₁₀ to C₂₂ saturate or unsaturated linear alkyl chain, more preferably a saturated C₁₂ to C₁₆ linear alkyl chain, most preferably C₁₂ linear alkyl chain (lauryl). The average number of moles of ethoxylation per mole of surfactant is m, m is preferably 2 to 4, most preferably 2.5 to 3.5.

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Further Surfactant

The aqueous liquid laundry detergent may comprises from 0 to 4wt% of further surfactants, for example, those described in Anionic Surfactants: Organic Chemistry edited by Helmut W. Stache (Marcel Dekker 1996).

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Examples of suitable further anionic detergent compounds are; alkyl sulphates, especially those obtained by sulphating linear or branched C₈ to C₁₈ alcohols; soaps; alkyl (preferably methyl) ester sulphonates, and mixtures thereof. Soaps are particularly preferred, preferably at a range from 0.5 to 2 wt%.

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Branched surfactant are preferably branched with methyl or ethyl groups.

Zwitterionic surfactant contain a linear C8 to C16 aliphatic alkyl chain and a formally positive and a formally negative charged atom within the surfactant molecule. Example zwitterionic surfactants are betaines. Zwitterionic surfactants are preferable present at levels less than 0.2wt%, most preferably at levels less than 0.05wt%, even more preferably absent from the formulation.

Sarcosinates, glycinate, taurinate are preferably absent from the formulation.

Polymers

The composition may comprise one or more further polymers. Examples are carboxymethylcellulose, polyetheramines, poly(ethylene glycol), poly(vinyl alcohol), polycarboxylates such as polyacrylates, maleic/acrylic acid copolymers and lauryl methacrylate/acrylic acid copolymers. Co-polymers as described in WO2014/082955 (Unilever) may be present.

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Polymers present to prevent dye deposition may be present, for example poly(vinylpyrrolidone), poly(vinylpyridine-N-oxide), and poly(vinylimidazole).

Random graft copolymers are preferred, preferably a polyvinyl acetate grafted polyethylene oxide copolymer, most preferably a polyethylene oxide backbone of molecular weight from 4000 to 8000, grafted with multiple polyvinylacetate side chains such that the weight ratio of the polyethylene backbone to polyvinyl acetate is from 35 to 65 and with no more than 1 grafting point per 50 ethylene oxide monomer units. This is commercially available as Sokalan PG101® (BASF).

Such polymers are preferably present at levels of less than 0.5 wt%.

The composition is preferably devoid of silicone polymers and polymers bearing quaternised N groups.

Builders and Sequestrants

The detergent compositions may also optionally contain relatively low levels of organic detergent builder or sequestrant material. Examples include the alkali metal, citrates, succinates, malonates, carboxymethyl succinates, carboxylates, polycarboxylates and polyacetyl carboxylates. Specific examples include sodium, potassium and lithium salts of oxydisuccinic acid, mellitic acid, benzene polycarboxylic acids, ethylene diamine tetra-acetic

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acid, diethylenetriamine-pentaacetic acid, alkyl- or alkenylsuccinic acid, nitrilotriacetic acid, and citric acid. Other examples are DEQUEST™, organic phosphonate type sequestering agents sold by Monsanto and alkanehydroxy phosphonates.

5 Other suitable organic builders include the higher molecular weight polymers and copolymers known to have builder properties. For example, such materials include appropriate polyacrylic acid, polymaleic acid, and polyacrylic/polymaleic acid copolymers and their salts, such as those sold by BASF under the name SOKALAN™.

10 The aqueous liquid detergent composition preferably comprises from 0.0.% to 2.0 wt% builder and sequesterant material. Citrate is most preferred.

The pH of the aqueous liquid detergent composition is preferably from 6.5 to 8.5, most preferably 6.8 to 7.5. The pH may be obtained by the addition of an alkali, such as NaOH,
15 KOH, trialkyl amine, alkanolamines and mixtures thereof.

Shading Dye

Dyes are described in *Color Chemistry Synthesis, Properties and Applications of Organic Dyes and Pigments*, (H Zollinger, Wiley VCH, Zürich, 2003) and, *Industrial Dyes Chemistry, Properties Applications*. (K Hunger (ed), Wiley-VCH Weinheim 2003).
20

Shading Dyes for use in laundry detergents preferably have an extinction coefficient at the maximum absorption in the visible range (400 to 700nm) of greater than $5000 \text{ L mol}^{-1} \text{ cm}^{-1}$, preferably greater than $10000 \text{ L mol}^{-1} \text{ cm}^{-1}$. The dyes are blue or violet in colour.

25 Preferred shading dye chromophores are azo, azine, anthraquinone, and triphenylmethane. Preferred mono-azo dyes contain a heterocyclic ring and are most preferably thiophene dyes. The mono-azo dyes are preferably alkoxylated and are preferably uncharged or anionically charged at pH=7. Alkoxylated thiophene dyes are discussed in WO/2013/142495
30 and WO/2008/087497.

The azine dye is preferably selected from sulphonated phenazine dyes and cationic phenazine dyes. Preferred examples are acid blue 98, acid violet 50, dye with CAS-No 72749-80-5, acid blue 59.

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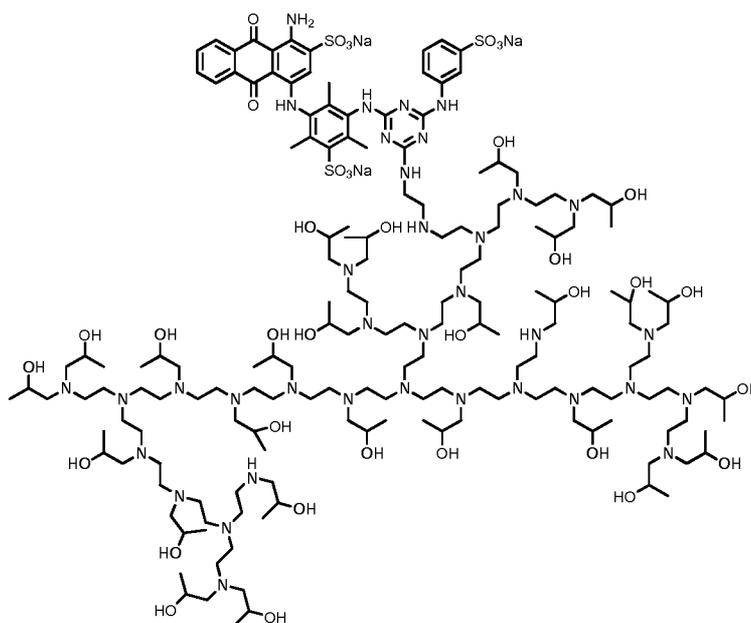
The shading dye is present in the composition in range from 0.0001 to 0.5 wt %, preferably 0.001 to 0.1 wt%. Depending upon the nature of the shading dye there are preferred ranges depending upon the efficacy of the shading dye which is dependent on class and particular efficacy within any particular class. As stated above the shading dye is a blue or violet shading dye.

A mixture of shading dyes may be used.

The shading dye is most preferably a reactive blue anthraquinone dye covalently linked to an alkoxyated polyethyleneimine. The alkoxylation is preferably selected from ethoxylation and propoxylation, most preferably propoxylation. Preferably 80 to 95 mol% of the N-H groups in the polyethylene imine are replaced with iso-propyl alcohol groups by propoxylation. Preferably, the polyethylene imine before reaction with the dye and the propoxylation has a molecular weight of 600 to 1800.

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An example structure of a preferred reactive anthraquinone covalently attached to a propoxyated polyethylene imine is:



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Preferred reactive anthraquinone dyes are: Reactive blue 1; Reactive blue 2; Reactive blue 4; Reactive blue 5; Reactive blue 6; Reactive blue 12; Reactive blue 16; reactive blue 19; Reactive blue 24 ; Reactive blue 27; Reactive blue 29; Reactive blue 36; Reactive blue 44; Reactive blue 46 ; Reactive blue 47; reactive blue 49; Reactive blue 50; Reactive blue 53;

Reactive blue 55; Reactive blue 61; Reactive blue 66; Reactive blue 68; Reactive blue 69; Reactive blue 74; Reactive blue 86; Reactive blue 93; Reactive blue 94; Reactive blue 101; Reactive blue 103; Reactive blue 114; Reactive blue 117; Reactive blue 125; Reactive blue 141; Reactive blue 142; Reactive blue 145; Reactive blue 149; Reactive blue 155; Reactive blue 164; Reactive blue 166; Reactive blue 177; Reactive blue 181; Reactive blue 185; Reactive blue 188; Reactive blue 189; Reactive blue 206; Reactive blue 208; Reactive blue 246; Reactive blue 247; Reactive blue 258; Reactive blue 261; Reactive blue 262; Reactive blue 263; and Reactive blue 172.

10 The dyes are listed according to Colour Index (Society of Dyers and Colourists/American Association of Textile Chemists and Colorists) classification.

The inventive formulation reduced the staining of dyes on neat contact with the fabric.

15 **Protease Enzyme**

Preferably, the composition comprises a protease enzyme at a level from 0.002 to 0.05 wt% pure protein. The combination of protease enzyme and alkyl ether carboxylate synergistically enhances cleaning. Protease enzymes hydrolyse bonds within peptides and proteins, in the laundry context this leads to enhanced removal of protein or peptide containing stains.

20 Examples of suitable proteases families include aspartic proteases; cysteine proteases; glutamic proteases; asparagine peptide lyase; serine proteases and threonine proteases. Such protease families are described in the MEROPS peptidase database (<http://merops.sanger.ac.uk/>). Serine proteases are preferred. Subtilase type serine proteases are more preferred. The term "subtilases" refers to a sub-group of serine protease according to Siezen et al., Protein Engng. 4 (1991) 719-737 and Siezen et al. Protein Science 6 (1997) 501 -523. Serine proteases are a subgroup of proteases characterized by having a serine in the active site, which forms a covalent adduct with the substrate. The subtilases may be divided into 6 sub-divisions, i.e. the Subtilisin family, the Thermitase family, the Proteinase K family, the Lantibiotic peptidase family, the Kexin family and the Pyrolysin family.

35 Examples of subtilases are those derived from Bacillus such as Bacillus lentus, B. alkalophilus, B. subtilis, B. amyloliquefaciens, Bacillus pumilus and Bacillus gibsonii described in; US7262042 and WO09/021867, and subtilisin lentus, subtilisin Novo, subtilisin Carlsberg, Bacillus licheniformis, subtilisin BPN', subtilisin 309, subtilisin 147 and subtilisin

168 described in WO89/06279 and protease PD138 described in (WO93/18140). Other useful proteases may be those described in W092/175177, WO01/016285, WO02/026024 and WO02/016547. Examples of trypsin-like proteases are trypsin (e.g. of porcine or bovine origin) and the Fusarium protease described in WO89/06270, W094/25583 and
5 WO05/040372, and the chymotrypsin proteases derived from Cellulomonas described in WO05/052161 and WO05/052146.

Further Examples of useful proteases are the variants described in: W092/19729, WO96/034946, WO98/201 15, WO98/201 16, WO99/01 1768, WO01/44452, WO03/006602,
10 WO04/03186, WO04/041979, WO07/006305, W01 1/036263, W01 1/036264, especially the variants with substitutions in one or more of the following positions: 3, 4, 9, 15, 27, 36, 57, 68, 76, 87, 95, 96, 97, 98, 99, 100, 101 , 102, 103, 104, 106, 1 18, 120, 123, 128, 129, 130, 160, 167, 170, 194, 195, 199, 205, 206, 217, 218, 222, 224, 232, 235, 236, 245, 248, 252 and 274 using the BPN' numbering. More preferred the subtilase variants may comprise the
15 mutations: S3T, V4I, S9R, A15T, K27R, *36D, V68A, N76D, N87S,R, *97E, A98S, S99G,D,A, S99AD, S101 G,M,R S103A, V104I,Y,N, S106A, G1 18V,R, H120D,N, N123S, S128L, P129Q, S130A, G160D, Y167A, R170S, A194P, G195E, V199M, V205I, L217D, N218D, M222S, A232V, K235L, Q236H, Q245R, N252K, T274A (using BPN' numbering).

20 Most preferably the protease is a subtilisin (EC 3.4.21.62).

Examples of subtilases are those derived from Bacillus such as Bacillus lentus, B. alkalophilus, B. subtilis, B. amyloliquefaciens, Bacillus pumilus and Bacillus gibsonii described in; US7262042 and WO09/021867, and subtilisin lentus, subtilisin Novo, subtilisin
25 Carlsberg, Bacillus licheniformis, subtilisin BPN', subtilisin 309, subtilisin 147 and subtilisin 168 described in WO89/06279 and protease PD138 described in (WO93/18140). Preferably the subtilisin is derived from Bacillus, preferably Bacillus lentus, B. alkalophilus, B. subtilis, B. amyloliquefaciens, Bacillus pumilus and Bacillus gibsonii as described in US 6,312,936 BI, US 5,679,630, US 4,760,025, US7,262,042 and WO09/021867. Most preferably the
30 subtilisin is derived from Bacillus gibsonii or Bacillus Lentus.

Suitable commercially available protease enzymes include those sold under the trade names Alcalase®, Blaze®; Duralase™, Durazym™, Release®, Release® Ultra, Savinase®, Savinase® Ultra, Primase®, Polarzyme®, Kannase®, Liquanase®, Liquanase® Ultra,

Ovozyme®, Coronase®, Coronase® Ultra, Neutrase®, Everlase® and Esperase® all could be sold as Ultra® or Eivity® (Novozymes A/S).

Those sold under the tradename Maxatase®, Maxacal®, Maxapem®, Properase®,
5 Purafect®, Purafect Prime®, Purafect Ox®, FN3®, FN4®, Excellase® and Purafect OXP®
by Genencor International.

Those sold under the tradename Maxatase®, Maxacal®, Maxapem®, Purafect®, Purafect
Prime®, Preferenz™, Purafect MA®, Purafect Ox®, Purafect OxP®, Puramax®,
10 Properase®, Effectenz™, FN2®, FN3®, FN4®, Excellase®, Opticlean® and Optimase®
(Danisco/DuPont), Axapem™ (Gist-Brocades N.V.),

Those available from Henkel/ Kemira, namely BLAP (sequence shown in Figure 29 of
US 5,352,604 with the following mutations S99D + S101R + S103A + V104I + G159S,
15 hereinafter referred to as BLAP), BLAP R (BLAP with S3T + V4I + V199M + V205I + L217D),
BLAP X (BLAP with S3T + V4I + V205I) and BLAP F49 (BLAP with S3T + V4I + A194P +
V199M + V205I + L217D) - all from Henkel/Kemira; and KAP (Bacillus alkalophilus subtilisin
with mutations A230V + S256G + S259N) from Kao.

20 Inclusion of protease in the formulation enhances cleaning.

Further Enzymes

One or more further enzymes are preferred present in a laundry composition of the invention
and when practicing a method of the invention.

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Preferably, the level of each enzyme in the laundry composition of the invention is from
0.0001 wt% to 0.1 wt% protein.

Preferably, the further enzyme is selected from: alpha-amylases; lipases; and, cellulases.

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Suitable lipases include those of bacterial or fungal origin. Chemically modified or protein
engineered mutants are included. Examples of useful lipases include lipases from *Humicola*
(synonym *Thermomyces*), e.g. from *H. lanuginosa* (*T. lanuginosus*) as described in
EP 258 068 and EP 305 216 or from *H. insolens* as described in WO 96/13580, a

35 *Pseudomonas* lipase, e.g. from *P. alcaligenes* or *P. pseudoalcaligenes* (EP 218 272),

P. cepacia (EP 331 376), *P. stutzeri* (GB 1,372,034), *P. fluorescens*, *Pseudomonas* sp. strain SD 705 (WO 95/06720 and WO 96/27002), *P. wisconsinensis* (WO 96/12012), a *Bacillus* lipase, e.g. from *B. subtilis* (Dartois et al. (1993), *Biochemica et Biophysica Acta*, 1131, 253-360), *B. stearothermophilus* (JP 64/744992) or *B. pumilus* (WO 91/16422).

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Other examples are lipase variants such as those described in WO 92/05249, WO 94/01541, EP 407 225, EP 260 105, WO 95/35381, WO 96/00292, WO 95/30744, WO 94/25578, WO 95/14783, WO 95/22615, WO 97/04079 and WO 97/07202, and WO 00/60063.

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Preferred commercially available lipase enzymes include Lipolase™ and Lipolase Ultra™, Lipex™ and Lipoclean™ (Novozymes A/S).

Suitable amylases (alpha and/or beta) include those of bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Amylases include, for example, alpha-amylases obtained from *Bacillus*, e.g. a special strain of *B. licheniformis*, described in more detail in GB 1,296,839, or the *Bacillus* sp. strains disclosed in WO 95/026397 or WO 00/060060. Commercially available amylases are Duramyl™, Termamyl™, Termamyl Ultra™, Natalase™, Stainzyme™, Fungamyl™ and BAN™ (Novozymes A/S), Rapidase™ and Purastar™ (from Genencor International Inc.).

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Further enzymes suitable for use are discussed in WO2009/087524, WO2009/090576, WO2009/107091, WO2009/111258, and WO2009/148983.

25 **Enzyme Stabilizers**

Any enzyme present in the composition may be stabilized using conventional stabilizing agents, e.g., a polyol such as propylene glycol or glycerol, a sugar or sugar alcohol, lactic acid, boric acid, or a boric acid derivative, e.g., an aromatic borate ester, or a phenyl boronic acid derivative such as 4-formylphenyl boronic acid, and the composition may be formulated as described in e.g., WO 92/19709 and WO 92/19708.

30

Where alkyl groups are sufficiently long to form branched or cyclic chains, the alkyl groups encompass branched, cyclic and linear alkyl chains. The alkyl groups are preferably linear or branched, most preferably linear.

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Fluorescent Agent

The composition preferably comprises a fluorescent agent (optical brightener). Fluorescent agents are well known and many such fluorescent agents are available commercially.

Usually, these fluorescent agents are supplied and used in the form of their alkali metal salts, for example, the sodium salts.

Preferred classes of fluorescer are: Di-styryl biphenyl compounds, e.g. Tinopal (Trade Mark) CBS-X, Di-amine stilbene di-sulphonic acid compounds, e.g. Tinopal DMS pure Xtra and Blankophor (Trade Mark) HRH, and Pyrazoline compounds, e.g. Blankophor SN.

10

Preferred fluorescers are: sodium 2 (4-styryl-3-sulphophenyl)-2H-naphthol[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' disulphonate, disodium 4,4'-bis{[(4-anilino-6-morpholino-1,3,5-triazin-2-yl)]amino} stilbene-2-2' disulphonate, and disodium 4,4'-bis(2-sulphostyryl)biphenyl.

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The total amount of the fluorescent agent or agents used in the composition is preferably from 0.0001 to 0.5 wt %, more preferably 0.005 to 2 wt %, most preferably 0.05 to 0.25 wt %.

The aqueous solution used in the method has a fluorescer present. The fluorescer is present in the aqueous solution used in the method preferably in the range from 0.0001 g/l to 0.1 g/l, more preferably 0.001 to 0.02 g/l.

20

Perfume

The composition most preferably comprises a perfume. The perfume is preferably in the range from 0.001 to 3 wt %, more preferably 0.05 to 0.5 wt%, most preferably from 0.1 to 1 wt %. Many suitable examples of perfumes are provided in the CFTA (Cosmetic, Toiletry and Fragrance Association) 1992 International Buyers Guide, published by CFTA Publications and OPD 1993 Chemicals Buyers Directory 80th Annual Edition, published by Schnell Publishing Co.

30

Preferably the perfume comprises at least one note (compound) from: alpha-isomethyl ionone, benzyl salicylate; citronellol; coumarin; hexyl cinnamal; linalool; Pentanoic acid, 2-methyl-, ethyl ester; octanal; benzyl acetate; 1,6-octadien-3-ol, 3,7-dimethyl-, 3-acetate; cyclohexanol, 2-(1,1-dimethylethyl)-, 1-acetate; delta-damascone; beta-ionone; verdyl acetate; dodecanal; hexyl cinnamic aldehyde; cyclopentadecanolide; benzeneacetic acid, 2-

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phenylethyl ester; amyl salicylate; beta-caryophyllene; ethyl undecylenate; geranyl anthranilate; alpha-irone; beta-phenyl ethyl benzoate; alpha-santalol; cedrol; cedryl acetate; cedryl formate; cyclohexyl salicylate; gamma-dodecalactone; and, beta phenylethyl phenyl acetate.

5

Useful components of the perfume include materials of both natural and synthetic origin. They include single compounds and mixtures. Specific examples of such components may be found in the current literature, e.g., in Fenaroli's Handbook of Flavor Ingredients, 1975, CRC Press; Synthetic Food Adjuncts, 1947 by M. B. Jacobs, edited by Van Nostrand; or
10 Perfume and Flavor Chemicals by S. Arctander 1969, Montclair, N.J. (USA).

It is commonplace for a plurality of perfume components to be present in a formulation. In the compositions of the present invention, it is envisaged that there will be four or more, preferably five or more, more preferably six or more or even seven or more different perfume
15 components.

The International Fragrance Association has published a list of fragrance ingredients (perfumes) in 2011. (<http://www.ifraorg.org/en-us/ingredients#.U7Z4hPldWzk>)

20 The Research Institute for Fragrance Materials provides a database of perfumes (fragrances) with safety information.

Some or all of the perfume may be encapsulated.

25 It is preferred that the laundry treatment composition does not contain a peroxygen bleach, e.g., sodium percarbonate, sodium perborate, and peracid.

The indefinite article "a" or "an" and its corresponding definite article "the" as used herein means at least one, or one or more, unless specified otherwise.

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An ethane or propane based alcohol substituted by 2 to 3 OH's groups, preferably selected from glycerol and Propylene glycol, is preferable present in the formulation at levels from 1 to 5 wt%.

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Experimental

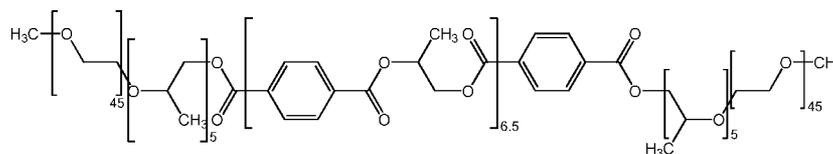
The following formulations were made:

Ingredient	Wt%	
	Control	inventive
Linear alkyl benzene sulfonate.	5.8	5.8
C12-C15 linear aliphatic alcohol with 7 moles of ethoxylation	4.4	4.4
Oleyl ether carboxylate	0.0	4.3
C12 alkyl ether sulfate with 3 mole equivalent of ethoxylation	4.4	4.4
SRP	1.0	1.0
EPEI	3.1	3.1
triethylamine	8.8	8.8
Sequesterant Dequest™ 2010	1.5	1.5
Propylene glycol	2.0	2.0
Fatty acid (Prifac™ 5908)	0.9	0.9
Acrylic acid/acrylic ester co-polymer	0.7	0.7
perfume	0.4	0.4
Citric acid	1.0	1.0
preservative	0.2	0.2
Fluorescer (Tinopal 5BMG-X ex BASF)	0.2	0.2
Demineralised water	Remainder	

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The EPEI (Ethoxylated PolyEthylene Imine) used was a PEI of 600 molecular weight with 20 moles of ethoxylate per NH on the base PEI; it is available as Sokalan HP20 ex BASF.

10 The SRP (Soil Removal Polymer) used was:



The SRP is as described in WO2014/019903 (Unilever).

15

The viscosity of the formulation were measured using a Paar Physica MCR300 is a commercial stress rheometer. The values are given in centipoise cP.

5 The results are presented in the table below for inventive formulations made oleyl ether carboxylate with different levels of ethoxylation and the control formulations

Formulation	Viscosity/cP
control	146
oleyl ether carboxylate with 2 moles of ethoxylation	291
oleyl ether carboxylate with 5 moles of ethoxylation	346
oleyl ether carboxylate with 8 moles of ethoxylation	286
oleyl ether carboxylate with 10 moles of ethoxylation	343

The inventive formulations containing the alkyl ether carboxylic acid have higher viscosity than the control.

CLAIMS

1. An aqueous liquid laundry detergent composition comprising:

- 5 (i) from 2 to 12 wt% of linear alkyl benzene anionic sulfonate surfactant;
- (ii) from 0.5 to 8 wt% of an ethoxylated alcohol non-ionic surfactant;
- 10 (iii) from 1 to 8 wt% of an alkoxyated polyethylene imine, preferably ethoxylated polyethylene imine;
- (iv) from 1 to 10 wt% of an alkyl ether carboxylic acid anionic surfactant of the following structure:



wherein:

R₂ is selected from saturated and mono-unsaturated C10 to C26 linear or branched alkyl chains; and wherein n is selected from: 2 to 20;

- 20 (v) from 0 to 4 wt% of a terephthalate polyester soil release polymer;
- (vi) from 0.0 to 6 wt% of an alkyl ether sulphate with a mole average of 1 to 4.5 moles of ethoxylation per surfactant molecule, wherein the weight fraction of
- 25 alkyl ether sulphate/non-ionic surfactant is less than 1.

2. An aqueous liquid laundry detergent composition according to claim 1, wherein the weight fraction of ethoxylated alcohol non-ionic surfactant/linear alkyl benzene anionic sulfonate surfactant is from 0.4 to 1.6.

- 30 3. An aqueous liquid laundry detergent composition according to claim 1 or 2, wherein the composition comprises from 2 to 4 wt% of the ethoxylated alcohol non-ionic surfactant.

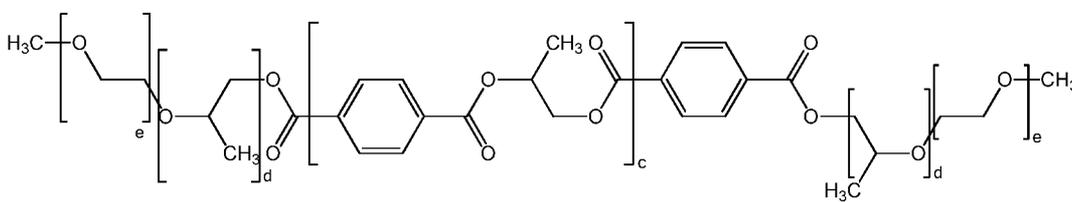
4. An aqueous liquid laundry detergent composition according to any one of the preceding claims, wherein the composition comprises from 2 to 6 wt% of the alkyl ether carboxylic acid anionic surfactant.

5. An aqueous liquid laundry detergent composition according to any one of the preceding claims, wherein the composition comprises from 4 to 8 wt% of the linear alkyl benzene anionic sulfonate surfactant.

6. An aqueous liquid laundry detergent composition according to any one of the preceding claims, wherein the alkoxyated polyethylene imine is an ethoxylated polyethylene imine.

7. An aqueous liquid laundry detergent composition according to any one of the preceding claims, wherein the composition comprises from 0.5 to 1.5 wt% of the terephthalate polyester soil release polymer.

8. An aqueous liquid laundry detergent composition according to claim 7, wherein the Terephthalate Polyester Soil Release Polymer is:



wherein c is from 4 to 9; d is from 1 to 3; e is from 40 to 50.

9. An aqueous liquid laundry detergent composition according to any one of the preceding claims, wherein n is selected from 7 to 13 and R₂ is selected from saturated and mono-unsaturated C16 to C18 linear alkyl chain.

10. An aqueous liquid laundry detergent composition according to any one of the preceding claims, wherein the ethoxylated alcohol non-ionic surfactant is a C12 to C15 primary aliphatic alcohol with 7 to 9 moles of ethylene oxide per mole of alcohol.

11. An aqueous liquid laundry detergent composition according to any one of the preceding claims, wherein the alkoxyated polyethylene imine has an average moles of alkoxylation (AO) per available NH in the unsubstituted polyethyleneimine backbone of from 16 to 26 and the unsubstituted polyethyleneimine backbone has a molecular weight from 500 to 800.

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12. A domestic method of treating a textile, the method comprising the steps of:

(i) treating a textile with from 1 g/L of an aqueous solution of the laundry detergent composition as defined in any one of the preceding claims; and,

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(ii) allowing said aqueous laundry detergent solution to remain in contact with the textile for 10 minutes to 2 days then rinsing and drying the textile.

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/053799

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C11D1/83 C11D3/37
 ADD. C11D1/06 C11D1/22 C11D1/29 C11D1/72
 According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
 Minimum documentation searched (classification system followed by classification symbols)
 C11D
 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
 EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 269 960 A (GRAY ROBERT L [US] ET AL) 14 December 1993 (1993-12-14) column 1, lines 10-12 column 2, line 59 - column 3, line 6 claims; examples	1-12
A	WO 2014/060235 A2 (UNILEVER PLC [GB]; UNILEVER NV [NL]; CONOPCO INC [US]) 24 April 2014 (2014-04-24) cited in the application page 1, lines 4-21; claims; examples	1-12
A	WO 2013/087284 A1 (UNILEVER PLC [GB]; UNILEVER NV [NL]; UNILEVER HINDUSTAN [IN]) 20 June 2013 (2013-06-20) page 1, lines 5-26; claims; examples	1-12
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Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier application or patent but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 24 April 2017	Date of mailing of the international search report 09/05/2017
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Péntek, Eric
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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/053799

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6 090 768 A (DELANEY SUSAN [US] ET AL) 18 July 2000 (2000-07-18) claims; examples -----	1-12

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No PCT/EP2017/053799

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			CN 103975049 A 06-08-2014
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