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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.



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LAUNDRY DETERGENT COMPOSITION

Field of 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 Laundry liquid formulation containing Linear Alkyl benzene sulfonate surfactant, Alkyl Ether Sulfate surfactant, and low levels of non-ionic surfactant and zwitterionic surfactant are ubiquitous. To enhance cleaning performance alkoxyated polyethylene imine polymers, preferably in combination with polyethylene terephthalate soil removal polymers. The addition of these polymers greatly reduces the viscosity of the formulation. Effective methods to increase the viscosity of the formulation are required, which do not reduce the surfactant level.

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WO201 3/087286 (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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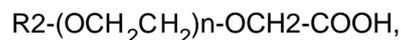
Summary of the Invention

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Surprisingly it is found that partial or complete replacement of the alkyl ether sulfate anionic surfactant with alkyl ether carboxylic acid anionic surfactant, increases the viscosity of the formulation.

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

- (i) from 2 to 10 wt%, preferably from 2.5 to 5 wt%, of linear alkyl benzene anionic sulfonate surfactant;
- 5 (ii) from 0.5 to 4 wt%, preferably 1.5 to 2.5 wt%, of zwitterionic surfactant selected from: amine oxide; and, carbobetaines;
- (iii) from 0.1 to 4 wt%, preferably 0.5 to 2 wt%, of an alkali metal salt, preferably NaCl;
- (iv) from 1 to 5 wt%, preferably 1.5 to 4 wt%, of an alkoxyated polyethylene imine, preferably ethoxylated polyethylene imine;
- 10 (v) 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:



15 wherein:

R₂ 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: 6 to 20, preferably 7 to 13, more preferably 8 to 12, most preferably 9.5 to 10.5;

- 20 (vi) from 0 to 10 wt%, preferably from 2.5 to 5 wt%, of alkyl ether sulfate anionic surfactant with 0.5 to 1.5 mole equivalent of ethoxylation, preferably 0.9 to 1.2;
- (vii) from 0 to 2 wt%, preferably 0.2 to 1wt% of a terephthalate polyester soil release polymer;
- (viii) from 0 to 4 wt%, preferably from 0 to 1wt%, of a non-ionic surfactant; and
- 25 (ix) from 0.0 to 0.2 wt%, preferably from 0.002 to 0.02 wt%, of a protease enzyme, wherein the laundry detergent composition comprises in total from 10 to 20 wt% of anionic surfactant.

In another aspect the present invention provides a domestic method of treating a textile, the
30 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,
- (ii) allowing said aqueous laundry detergent solution to remain in contact with the textile
35 for 10 minutes to 2 days then rinsing and drying the textile.

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 313K. The main wash time is preferably 5 to 30 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.

Detailed Description of the Invention

Linear alkyl benzene sulfonate

Weights of Linear alkyl benzene sulfonate are calculated as the protonated form. The linear 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 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.

Alkyl ether sulfate

Weights of alkyl ether sulfate are calculated as the protonated form, $\text{Ri}-(\text{OCH}_2\text{CH}_2)_m-\text{OSO}_3\text{H}$. Preferably Ri 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 0.5 to 1.5.

Alkyl ether carboxylic acid

Weights of alkyl ether carboxylic acid are calculated as the protonated form,

R₂-(OCH₂CH₂)_n-OCH₂COOH . They 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.

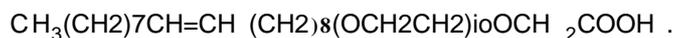
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The alkyl chain may be aliphatic or contain one cis or trans double bond.

The alkyl chain is preferably selected from CH₃(CH₂)₅, CH₃(CH₂)₇, CH₃(CH₂)₇CH=CH(CH₂)₈.

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

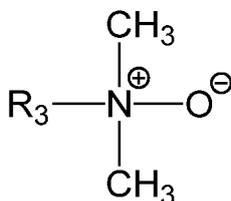


15 Alkyl ether carboxylic acid are available from Kao (Akypo®), Huntsman (Empicol®) and Clariant (Emulsogen®).

Zwitterionic surfactant

20 The zwitterionic surfactant contains a linear C8 to C16 aliphatic alkyl chain and a positive and negative charged atom within the surfactant molecule. Preferred zwitterionic surfactants are betaines and amine oxides.

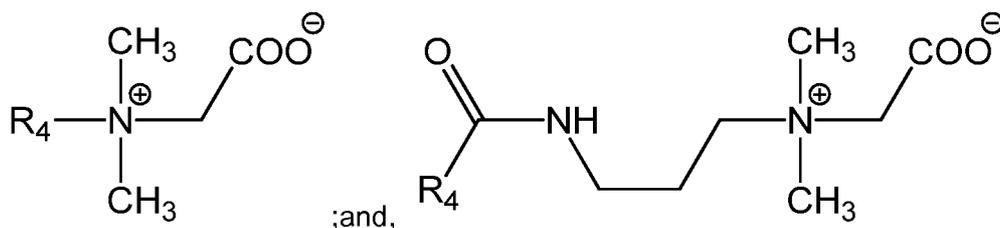
The amine oxide is preferably of the structure:



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Preferably R₃ is C12-C14, most preferably C12 (lauryl). Amine Oxides are available from Huntsman, for example, Empigen® OB.

30 The betaine is preferably a carbobetaine. The carbobetaine is preferably selected from the structures:



Preferably R_4 is C12-C14, most preferably C12 (lauryl). Betaines are available from
 Huntsman, for example Empigen® BB. Cocoamidopropyl betaine (Cas-No 61789-40-0) is
 5 most preferred.

The zwitterionic is most preferably a carbobetaine.

Non-ionic surfactant

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The aqueous liquid laundry detergent may comprise Non-ionic surfactant, preferably an alkyl
 ethoxylated non-ionic surfactant.

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Suitable nonionic detergent compounds which may be used include, in particular, the
 reaction products of compounds having an aliphatic hydrophobic group and a reactive
 hydrogen atom, for example, aliphatic alcohols, acids or amides, especially ethylene oxide
 either alone or with propylene oxide. The preferred nonionic detergent compounds are the
 condensation products of aliphatic C_s to C_{15} primary or secondary linear or branched
 alcohols with ethylene oxide.

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Preferably the alkyl ethoxylated non-ionic surfactant is a C_s to C_{15} primary alcohol with a
 mole average ethoxylation of 7EO to 9EO units.

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Preferably the fraction (weight% of non-ionic)/(weight% of anionic surfactant) is from 0 to
 0.2, more preferably 0 to 0.05. Most preferably the formulation does not contain non-ionic.

Further Surfactant

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The aqueous liquid laundry detergent may comprises from 0 to 4wt% of further surfactants,
 for example thos described in "Surface Active Agents" Vol. 1, by Schwartz & Perry,
 Interscience 1949, Vol. 2 by Schwartz, Perry & Berch, Interscience 1958, in the current

edition of "McCutcheon's Emulsifiers and Detergents" published by Manufacturing Confectioners Company or in "Tenside-Taschenbuch", H. Stache, 2nd Edn., Carl Hauser Verlag, 1981 or in Anionic Surfactants: Organic Chemistry edited by Helmut W. Stache (Marcel Dekker 1996) .

5

Examples of suitable further anionic detergent compounds are; alkyl sulphates, especially those obtained by sulphating linear or branched **C_s** to **C_{ie}** alcohols; soaps; alkyl (preferably methyl) ester sulphonates, and mixtures thereof.

10 **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 about 300 to about 10000 weight average molecular weight and is preferably about 600.

20

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.

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

Terephthalate Polyester Soil Release Polymer

30 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
35 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.

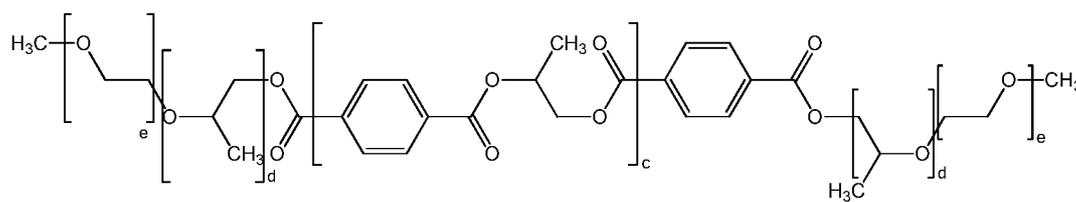
- 5 Preferred structure are $-(Z)_a-0-OC-Ar-CO-$ $_b$ and $(Z)_a-0-OC-[Ar-CO-0-C_3H_6-0-OC]_b-Ar-CO-0-(Z)_a$, where Ar is selected from 1,4 substituted phenylene and 1,3 substituted phenylene substituted in the 5 position with a sulphonates (SO_3^-) group; Z is selected from ethoxy;propoxy; and mixtures of ethoxy and propoxy; a is from 5 to 100 and b from 2 to 40. C3H6 is i-propyl.

10

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.

20 Polymers

The composition may comprise one or more further polymers. Examples are carboxymethylcellulose, poly (ethylene glycol), poly(vinyl alcohol), polycarboxylates such as polyacrylates, maleic/acrylic acid copolymers and lauryl methacrylate/acrylic acid copolymers.

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

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

- 30 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 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.

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™.

If utilised, the aqueous liquid laundry detergent formulation comprise from 0.1% to 2.0 wt% builder and sequesterant material. Citrate is most preferred.

Shading Dye

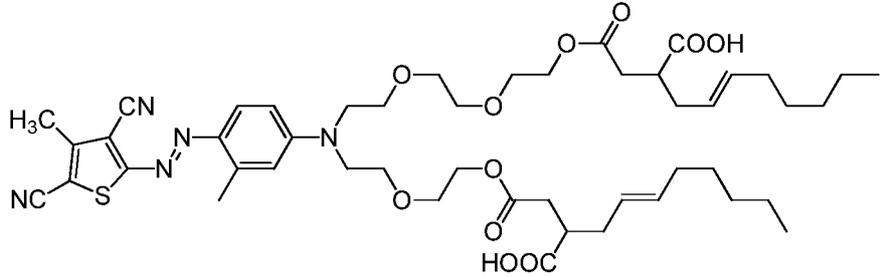
Dyes are described in *Color Chemistry Synthesis, Properties and Applications of Organic Dyes and Pigments*, (H Zollinger, Wiley VCH, Zurich, 2003) and, *Industrial Dyes Chemistry, Properties Applications*. (K Hunger (ed), Wiley-VCH Weinheim 2003).

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 L mol⁻¹ cm⁻¹, preferably greater than 10000 L mol⁻¹ cm⁻¹. The dyes are blue or violet in colour.

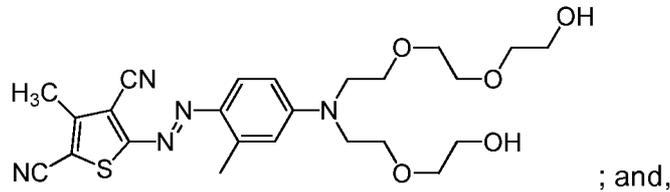
Preferred shading dye chromophores are azo, azine, anthraquinone, and triphenylmethane.

Preferred mono-azo dyes contain a heterocyclic ring and are most preferably thiophene dyes. The mono-azo dyes are preferably alkoxyated and are preferably uncharged or

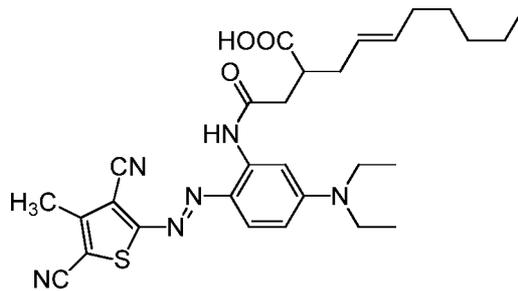
anionically charged at pH=7. Alkoxyated thiophene dyes are discussed in WO/2013/142495 and WO/2008/087497. Preferred examples of thiophene dyes are shown below:



5



; and,



.

10 Azine dye are 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.

15 The shading dye is present 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.

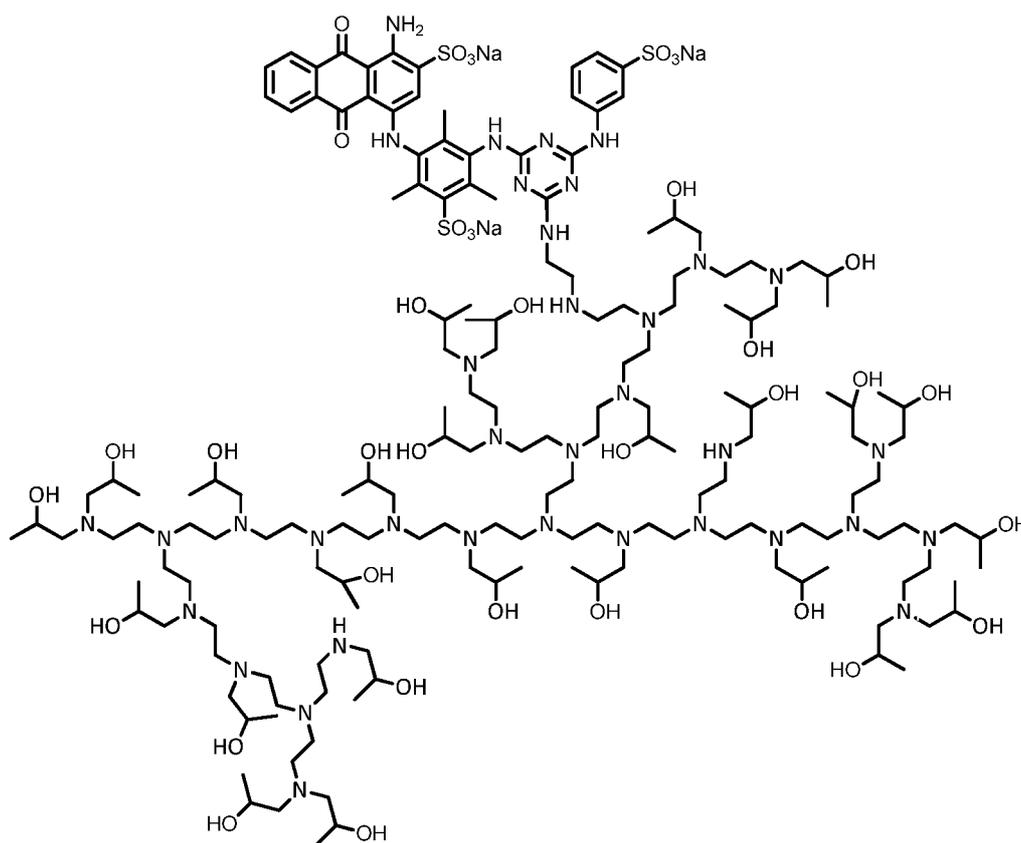
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A mixture of shading dyes may be used.

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.

- 10 An example structure of a preferred reactive anthraquinone covalently attached to a propoxylated polyethylene imine is:



- 15 (Structure I).

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
5 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.

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

Protease Enzyme

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Protease enzymes hydrolyse bonds within peptides and proteins, in the laundry context this
leads to enhanced removal of protein or peptide containing stains. Examples of suitable
proteases families include aspartic proteases; cysteine proteases; glutamic proteases;
asparagine peptide lyase; serine proteases and threonine proteases. Such protease families
20 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,
25 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.

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Examples of subtilases are those derived from Bacillus such as Bacillus lentus, B.
30 alkalophilus, B. subtilis, B. amyloliquefaciens, Bacillus pumilus and Bacillus gibsonii
described in; US7262042 and WO99/021867, 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
35 and WO02/016547. Examples of trypsin-like proteases are trypsin (e.g. of porcine or bovine

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origin) and the *Fusarium* protease described in WO89/06270, WO94/25583 and WO05/040372, and the chymotrypsin proteases derived from *Cellulomonas* described in WO05/052161 and WO05/052146.

5 Further Examples of useful proteases are the variants described in: WO92/19729, WO96/034946, WO98/201 15, WO98/201 16, WO99/01 1768, WO01/44452, WO03/006602, 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,
10 160, 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 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, G 1 18V,R, H120D,N, N123S, S128L, P129Q, S130A, G160D, Y167A, R170S, A194P, G195E, V199M, V205I, L217D,
15 N218D, M222S, A232V, K235L, Q236H, Q245R, N252K, T274A (using BPN' numbering).

Most preferably the protease is a subtilisins (EC 3.4.21 .62).

Examples of subtilases are those derived from *Bacillus* such as *Bacillus lentus*,
20 *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). Preferably the subtilisin is derived from *Bacillus*, preferably *Bacillus lentus*, *B. alkalophilus*, *B. subtilis*,
25 *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 subtilisin is derived from *Bacillus gibsonii* or *Bacillus Lentus*.

Suitable commercially available protease enzymes include those sold under the trade names
30 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 Evity® (Novozymes A/S).

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

- 5 Those sold under the tradename Maxatase®, Maxacal®, Maxapem®, Purafect®, Purafect Prime®, PreferenzTm, Purafect MA®, Purafect Ox®, Purafect OxP®, Puramax®, Properase®, EffectenzTm, FN2®, FN3®, FN4®, Excellase®, Opticlean® and Optimase® (Danisco/DuPont), Axapem™ (Gist-Brocades N.V.),
- 10 Those available from Henkel/Kemira, namely BLAP (sequence shown in Figure 29 of US 5,352,604 with the following mutations S99D + S101 R + S103A + V 104I + G 159S, 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
- 15 with mutations A230V + S256G + S259N) from Kao.

Inclusion of protease in the formulation enhances cleaning.

Further Enzymes

20

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

Preferably the level of each enzyme in the laundry composition of the invention is from

25 0.0001 wt% to 0.1 wt% protein.

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

Suitable lipases include those of bacterial or fungal origin. Chemically modified or protein

30 engineered mutants are included. Examples of useful lipases include lipases from *Humicola* (synonym *Thermomyces*), e.g. from *H. lanuginosa* (*T. lanuginosus*) as described in EP 258 068 and EP 305 216 or from *H. insolens* as described in WO 96/13580, a *Pseudomonas* lipase, e.g. from *P. alcaligenes* or *P. pseudoalcaligenes* (EP 218 272), *P. cepacia* (EP 331 376), *P. stutzeri* (GB 1,372,034), *P. fluorescens*, *Pseudomonas* sp. strain SD 705 (WO

35 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).

Other examples are lipase variants such as those described in WO 92/05249,
5 WO 94/01 541 , 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.

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

The method of the invention may be carried out in the presence of phospholipase classified
as EC 3.1 .1.4 and/or EC 3.1 .1.32. As used herein, the term phospholipase is an enzyme
which has activity towards phospholipids.

15

Phospholipids, such as lecithin or phosphatidylcholine, consist of glycerol esterified with two
fatty acids in an outer (sn-1) and the middle (sn-2) positions and esterified with phosphoric
acid in the third position; the phosphoric acid, in turn, may be esterified to an amino-alcohol.
Phospholipases are enzymes which participate in the hydrolysis of phospholipids. Several
20 types of phospholipase activity can be distinguished, including phospholipases **A_i** and **A₂**
which hydrolyze one fatty acyl group (in the sn-1 and sn-2 position, respectively) to form
lysophospholipid; and lysophospholipase (or phospholipase B) which can hydrolyze the
remaining fatty acyl group in lysophospholipid. Phospholipase C and phospholipase D
(phosphodiesterases) release diacyl glycerol or phosphatidic acid respectively.

25

The method of the invention may be carried out in the presence of cutinase classified in EC
3.1 .1.74. The cutinase used according to the invention may be of any origin. Preferably
cutinases are of microbial origin, in particular of bacterial, of fungal or of yeast origin.

30 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.).

5 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*, *Thielavia terrestris*, *Myceliophthora thermophila*, and *Fusarium oxysporum* disclosed in US 4,435,307, US 5,648,263,
10 US 5,691,178, US 5,776,757, WO 89/09259, WO 96/029397, and WO 98/012307. Commercially available cellulases include Celluzyme™, Carezyme™, Celluclean™, Endolase™, Renozyme™ (Novozymes A/S), Clazinase™ and Puradax HA™ (Genencor International Inc.), and KAC-500(B)™ (Kao Corporation). Celluclean™ is preferred.

15 Suitable peroxidases/oxidases include those of plant, bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Examples of useful peroxidases include peroxidases from *Coprinus*, e.g. from *C. cinereus*, and variants thereof as those described in WO 93/24618, WO 95/10602, and WO 98/15257. Commercially available peroxidases include Guardzyme™ and Novozym™ 51004 (Novozymes A/S).

20 Further enzymes suitable for use are discussed in WO2009/087524, WO2009/090576, WO2009/1 07091, WO2009/1 11258, and WO2009/1 48983.

Enzyme Stabilizers

25 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
30 as described in e.g., WO 92/19709 and WO 92/19708.

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.

Fluorescent Agent

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

- 5 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
10 Blankophor (Trade Mark) HRH, and Pyrazoline compounds, e.g. Blankophor SN.

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-
15 triazin-2-yl)]amino} stilbene-2-2' disulphonate, and disodium 4,4'-bis(2-sulphostyryl)biphenyl.

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 %.

- 20 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.

Perfume

- 25 The composition 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 CTFA (Cosmetic, Toiletry and Fragrance Association) 1992 International Buyers Guide, published by CFTA Publications and OPD
30 1993 Chemicals Buyers Directory 80th Annual Edition, published by Schnell Publishing Co.

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;
35 cyclohexanol, 2-(1,1-dimethylethyl)-, 1-acetate; delta-damascone; beta-ionone; verdyl

acetate; dodecanal; hexyl cinnamic aldehyde; cyclopentadecanolide; benzeneacetic acid, 2-phenylethyl ester; amyl salicylate; beta-caryophyllene; ethyl undecylenate; geranyl anthranilate; alpha-irone; beta-phenyl ethyl benzoate; alpa-santalol; cedrol; cedryl acetate; cedry formate; cyclohexyl salicyate; gamma-dodecalactone; and, beta phenylethyl phenyl acetate.

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 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 components.

In perfume mixtures preferably 15 to 25 wt% are top notes. Top notes are defined by Poucher (Journal of the Society of Cosmetic Chemists 6(2):80 [1955]). Preferred top-notes are selected from citrus oils, linalool, linalyl acetate, lavender, dihydromyrcenol, rose oxide and cis-3-hexanol.

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

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

Perfume top note may be used to cue the whiteness and brightness benefit of the invention.

Some or all of the perfume may be encapsulated, typical perfume components which it is advantageous to encapsulate, include those with a relatively low boiling point, preferably those with a boiling point of less than 300, preferably 100-250 Celsius. It is also advantageous to encapsulate perfume components which have a low CLog P (ie. those which will have a greater tendency to be partitioned into water), preferably with a CLog P of

less than 3.0. These materials, of relatively low boiling point and relatively low CLog P have been called the "delayed blooming" perfume ingredients and include one or more of the following materials: allyl caproate, amyl acetate, amyl propionate, anisic aldehyde, anisole, benzaldehyde, benzyl acetate, benzyl acetone, benzyl alcohol, benzyl formate, benzyl
5 iso valerate, benzyl propionate, beta gamma hexenol, camphor gum, laevo-carvone, d-carvone, cinnamic alcohol, cinamyl formate, cis-jasmone, cis-3-hexenyl acetate, cuminic alcohol, cyclal c, dimethyl benzyl carbinol, dimethyl benzyl carbinol acetate, ethyl acetate, ethyl aceto acetate, ethyl amyl ketone, ethyl benzoate, ethyl butyrate, ethyl hexyl ketone, ethyl phenyl acetate, eucalyptol, eugenol, fenchyl acetate, flor acetate (tricyclo
10 decenyl acetate) , frutene (tricyclo decenyl propionate) , geraniol, hexenol, hexenyl acetate, hexyl acetate, hexyl formate, hydratropic alcohol, hydroxycitronellal, indone, isoamyl alcohol, iso menthone, isopulegyl acetate, isoquinolone, ligustral, linalool, linalool oxide, linalyl formate, menthone, menthyl acetphenone, methyl amyl ketone, methyl anthranilate, methyl benzoate, methyl benyl acetate, methyl eugenol, methyl heptenone, methyl heptine
15 carbonate, methyl heptyl ketone, methyl hexyl ketone, methyl phenyl carbiny acetate, methyl salicylate, methyl-n-methyl anthranilate, nerol, octalactone, octyl alcohol, p-cresol, p-cresol methyl ether, p-methoxy acetophenone, p-methyl acetophenone, phenoxy ethanol, phenyl acetaldehyde, phenyl ethyl acetate, phenyl ethyl alcohol, phenyl ethyl dimethyl carbinol, prenyl acetate, propyl bornate, pulegone, rose oxide, safrole, 4-terpinenol, alpha-
20 terpinenol, and /or viridine. 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 components from the list given of delayed blooming perfumes given above present in the perfume.

25

Another group of perfumes with which the present invention can be applied are the so-called 'aromatherapy' materials. These include many components also used in perfumery, including components of essential oils such as Clary Sage, Eucalyptus, Geranium, Lavender, Mace Extract, Neroli, Nutmeg, Spearmint, Sweet Violet Leaf and Valerian.

30

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
35 means at least one, or one or more, unless specified otherwise.

Experimental

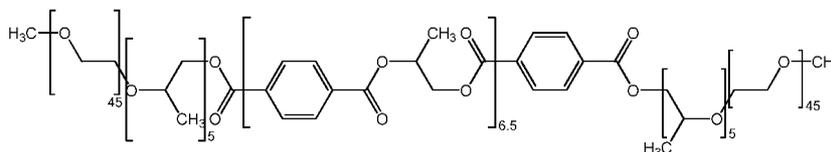
The following formulations were made with varying level of salt and SRP addition.

Ingredient	Weight% (pure material)		
	Control	F1	F2
Linear alkyl benzene sulfonate.	3.0	3.0	3.0
C12 alkyl ether sulfate with 1 mole equivalent of ethoxylation	9.0	4.5	4.5
Oleyl ether carboxylate with 10 mole equivalent of ethoxylation	0.0	4.5	0.0
Lauryl ether carboxylate with 10 mole equivalent of ethoxylation	0.0	0.0	4.5
Cocamidopropyl Betaine	2.0	2.0	2.0
EPEI	1.6	1.6	1.6
triethylamine	1.0	1.0	1.0
perfume	0.4	0.4	0.4
Citric acid	0.3	0.3	0.3
NaOH (to pH =8.0)	0.3	0.3	0.3
Fluorescer (Tinopal CBS-X ex BASF)	0.1	0.1	0.1
NaCl	See text		
SRP	See text		
Demineralised water	<i>remainder</i>		

5

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) was used at a level of 0.0 wt% and 0.5 wt%. The SRP used was:



- 15 The SRP is as described in WO201 4/01 9903 (Unilever).

The viscosity of the formulation were measured using a Paar Physica MCR300 is a commercial stress rheometer.

The results are presented in the table below for formulation in the absence of the SRP polymer (0.0 wt%).

Weight % NaCl	Viscosity / N s m ⁻² x10 ⁻³		
	Control <i>reference</i>	F1 <i>inventive</i>	F2 <i>inventive</i>
1.0	53	237	186
1.5	151	1170	730
2.0	385	2910	1680

5

The inventive formulation F1 and F2 containing the alkyl ether carboxylic acid have higher viscosity than the control with sodium lauryl ether sulfate alone.

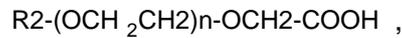
10 The results are presented in the table below for formulation in the presence of the SRP polymer (0.5 wt%).

Weight % NaCl	Viscosity / N s m ⁻² x10 ⁻³		
	Control <i>reference</i>	F1 <i>inventive</i>	F2 <i>inventive</i>
2.0	345	1100	805

15 The inventive formulation F1 and F2 containing the alkyl ether carboxylic acid have higher viscosity than the control with sodium lauryl ether sulfate alone.

CLAIMS

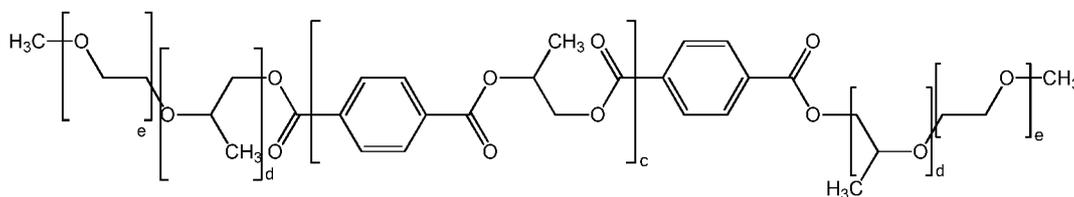
1. An aqueous liquid laundry detergent composition comprising:
- (i) from 2 to 10 wt% of a linear alkyl benzene anionic sulfonate surfactant;
- 5 (ii) from 0.5 to 4 wt% of zwitterionic surfactant selected from: amine oxide and carbobetaines;
- (iii) from 0.1 to 4 wt% of an alkali metal salt;
- (iv) from 1 to 5 wt% of an alkoxyated polyethylene imine;
- (v) from 1 to 10 wt% of an alkyl ether carboxylic acid anionic surfactant of the
- 10 following structure:



wherein:

- 15 R2 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 6 to 20;
- (vi) from 0 to 10 wt% of an alkyl ether sulfate anionic surfactant with 0.5 to 1.5 mole
- 20 equivalent of ethoxylation;
- (vii) from 0 to 2 wt% of a terephthalate polyester soil release polymer;
- (viii) from 0 to 4 wt% of a non-ionic surfactant; and,
- (ix) from 0.0 to 0.2 wt% of a protease enzyme, wherein the laundry detergent
- 25 composition comprises in total from 10 to 20 wt% of anionic surfactant.
2. An aqueous liquid laundry detergent composition according to claim 1, wherein the composition comprises from 1.5 to 2.5 wt% of a zwitterionic surfactant and from 0.5 to 2 wt% of an alkali metal salt.
- 30 3. An aqueous liquid laundry detergent composition according to claim 1 or 2, wherein the composition comprises from 2.5 to 5 wt% of an alkyl ether sulfate anionic surfactant.

4. An aqueous liquid laundry detergent composition according to any one of the preceding claims, wherein the composition comprises from 3 to 5 wt% of an 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 2.5 to 5 wt% of a 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 0.2 to 1 wt% of a terephthalate polyester soil release polymer.
8. An aqueous liquid laundry detergent composition according to claim 7, wherein the Terephthalate Polyester Soil Release Polymer is:



20

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 8 to 12, 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 alkali metal salt is sodium chloride.

30

11. 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,
 - (ii) allowing said aqueous laundry detergent solution to remain in contact with the
- 5 textile for 10 minutes to 2 days then rinsing and drying the textile.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/053522

A. CLASSIFICATION OF SUBJECT MATTER
INV. CIIDI/83 CIIDI/94 C11D3/37
 ADD.
 According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
 Minimum documentation searched (classification system followed by classification symbols)
C1D

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.
Y	wo 2014/019903 AI (UNI LEVER PLC [GB] ; UNI LEVER NV [NL] ; CONOPCO INC DBA UNI LEVER [US]) 6 February 2014 (2014-02-06) cited in the applicati on tabl es 5,6 page 24, lines 1-15 -----	1-11
Y	wo 2013/087284 AI (UNI LEVER PLC [GB] ; UNI LEVER NV [NL] ; UNI LEVER HINDUSTAN [IN] ; CONOPCO) 20 June 2013 (2013-06-20) tabl es 1,2 page 2, line 14 - page 3, line 5 page 4, lines 15-20 page 8, lines 18-20 page 17, lines 9-13 -----	1-11
Y	EP 1 739 161 AI (KA0 CHEMICALS GMBH [DE]) 3 January 2007 (2007-01-03) paragraph [0010] -----	1-11

Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance	"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 18 April 2017	Date of mailing of the international search report 26/04/2017
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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 Martti n, Emmel ine
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No PCT/EP2017/053522
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		WO 2014019903 A1	06-02-2014

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		EP 1739161 A1	03-01-2007
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