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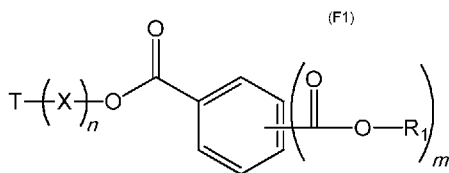
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(54) Title: WHITENING COMPOSITION



(57) Abstract: The invention provides a laundry cleaning composition comprising:-  
i) from 0.2 to 20 wt.% of an alkoxyated dispersant of the following structure (F1): wherein: X is selected from: ethoxy; and mixtures of ethoxy and propoxy groups where the number of ethoxy groups is greater than the number of propoxy groups, and wherein n is from 6 to 70; m is selected from: 2 and 3; R<sub>1</sub> is selected from: uncharged C12 to C20 alkyl groups; uncharged aryl groups; and, uncharged alkyl-aryl groups wherein the alkyl group of the alkyl-aryl is a saturated linear or branched C1 to C3; T is selected from: H; CH<sub>3</sub>; SO<sub>3</sub><sup>-</sup>; CH<sub>2</sub>COO<sup>-</sup>; PO<sub>3</sub><sup>2-</sup>; C<sub>2</sub>H<sub>5</sub>; n-propyl, i-propyl; n-butyl; t-butyl; and, sulfosuccinate; (ii) from 0 to 50 wt.% surfactant, other than the alkoxyated dispersant; (iii) an active ingredient selected from one or more of the following: from 0.001 to 3 wt.% perfume; from 0.0001 to 0.5 wt.% of fluorescent agent; and, from 0.0001 wt.% to 0.1 wt.% of an enzyme; The invention further relates to a domestic method of treating a textile comprising treatment of the textile with an aqueous liquor comprising said alkoxyated dispersant.



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## WHITENING COMPOSITION

### Field of Invention

The present invention concerns a laundry cleaning composition.

5

### Background of the Invention

There is a desire to use less water in the domestic laundering of clothes. This may be achieved by reducing the number of water rinses done after the initial washing. Reducing the number of rinses increases the redeposition of soil removed in the wash, thereby reducing the overall cleaning. The problem is exacerbated by the presence of human sebum on garments and in the wash liquor, which serves to enhance the deposition of soil in the wash. There is a need for improved dispersants to prevent the deposition of soil present in the wash liquor onto the fabric. Such ingredients are preferably biodegradable and increase stain removal.

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### Summary of the Invention

There is a need for technologies to reduce redeposition and enhance cleaning in domestic laundry products.

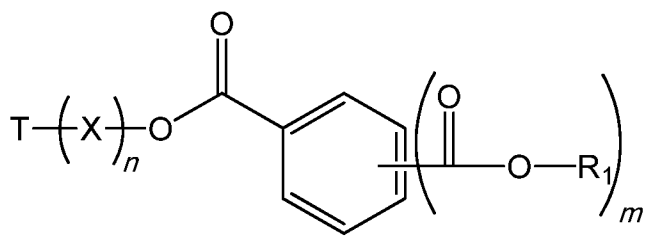
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We have found that selected alkoxyated dispersants (AD) when incorporated into laundry detergents enhance whiteness and brightness of garments during domestic laundry.

In a first aspect the present invention provides a laundry cleaning composition comprising:

20

- (i) from 0.2 to 20 wt.%, preferably 0.5 to 12 wt.%, most preferably 1 to 10 wt.% of an alkoxyated dispersant of the following structure:



wherein:

- 2 -

X is selected from: ethoxy; and mixtures of ethoxy and propoxy groups, wherein the number of ethoxy groups is greater than the number of propoxy groups, and wherein  $n$  is from 6 to 70;

$m$  is selected from: 2 and 3;

5  $R_1$  is selected from: uncharged C12 to C20 alkyl groups; uncharged aryl groups; and, uncharged alkyl-aryl groups wherein the alkyl group of the alkyl-aryl is a saturated linear or branched C1 to C3;

T is selected from: H; CH<sub>3</sub>; SO<sub>3</sub><sup>-</sup>; CH<sub>2</sub>COO<sup>-</sup>; PO<sub>3</sub><sup>2-</sup>; C<sub>2</sub>H<sub>5</sub>; n-propyl, i-propyl; n-butyl; t-butyl; and, sulfosuccinate;

10

(ii) from 0 to 50 wt.% surfactant, other than the alkoxyated dispersant; and,

(iii) an active selected from one or more of the following: from 0.001 to 3 wt.% perfume; from 0.0001 to 0.5 wt.% of fluorescent agent; and, from 0.0001 wt.% to  
15 0.1 wt% of an enzyme.

Preferably  $R_1$  is an alkyl-aryl group in the alkoxyated dispersant structure.

Preferably T is not H in the alkoxyated dispersant structure.

Preferably X is ethoxy in the alkoxyated dispersant structure.

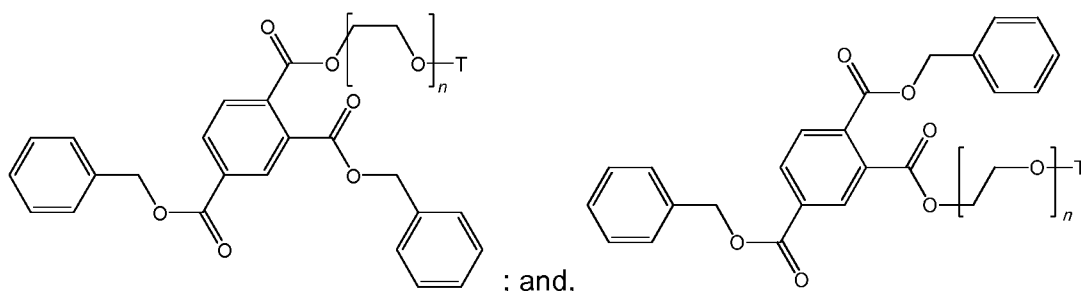
20 Preferably  $n$ , the mole average number of alkoxy groups, is from 6 to 40, more preferably from 9 to 30, most preferably from 10 to 20 in the alkoxyated dispersant structure.

Preferably T is CH<sub>3</sub> in the alkoxyated dispersant structure.

Preferably  $R_1$  is selected from: phenylethyl and benzyl. More preferably  $R_1$  is benzyl.

Preferably the alkoxyated dispersant is selected from:

25



A preferred laundry cleaning composition comprise surfactant, other than the alkoxyated dispersant, at a level of from 4 to 40 wt.%, more preferably from 4 to 35 wt.%, most  
30 preferably from 6 to 30 wt.%.

Preferably the surfactant, other than the alkoxyated dispersant, comprises anionic and/or non-ionic surfactants.

5 More preferably the weight fraction of non-ionic surfactant to anionic surfactant is from 0 to 0.3. This means that non-ionic surfactant can be present (or it may be absent if the weight fraction is 0), but if non-ionic surfactant is present, then the weight fraction of the non-ionic surfactant is preferably at most 30% of the total weight of anionic surfactant + non-ionic surfactant, wherein the alkoxyated dispersant is not considered a surfactant as defined herein.

10

Preferably the anionic surfactant is selected from: linear alkyl benzene sulphonates; alkyl sulphates; alkyl ether sulphates; and mixtures thereof.

15 If a non-ionic surfactant is present, then preferably the non-ionic surfactant is an alcohol ethoxylate, more preferably an C<sub>10</sub>-C<sub>18</sub> alcohol ethoxylate having an average of 3-10 moles of ethylene oxide, most preferably an C<sub>12</sub>-C<sub>15</sub> alcohol ethoxylate having an average of 5-9 moles of ethylene oxide.

20 The laundry cleaning composition is preferably an aqueous laundry liquid detergent composition. Preferably the pH of the aqueous liquid detergent composition is from 6 to 8.5, more preferably from 6.5 to 7.5, even more preferably from 6.8 to 7.2, most preferably 7.0.

25 Preferably the active ingredient is an enzyme and comprises one or more of the following: proteases, alpha-amylases, cellulases, lipases, peroxidases/oxidases, pectate lyases, and mannanases, or mixtures thereof. More preferably the enzyme is a protease, most preferably a subtilase type serine protease.

30 In a second aspect, the invention provides a domestic method of treating a textile, the method comprising the steps of:

(i) treating a textile with an aqueous solution of the alkoxyated dispersant as defined in the first aspect of the invention;  
the aqueous solution comprising from 10 ppm to 5000 ppm, preferably from 100  
35 ppm to 1000 ppm, of the alkoxyated dispersant as defined herein; and, 0 to 6 g/L,

- 4 -

preferably from 0.5 to 6 g/L, more preferably from 1 to 5 g/L of a surfactant, other than the alkoxyated dispersant; and,

(ii) optionally rinsing and drying the textile;

- 5 wherein in the method, one or more of an active ingredient selected from perfume, fluorescent agent and enzyme is present in the aqueous solution of the alkoxyated dispersant, wherein if present, the level of the perfume in the aqueous solution is from 0.1 to 100 ppm; preferably from 1 to 10ppm.
- 10 wherein if present, the level of the fluorescent agent in the aqueous solution is from 0.0001 g/l to 0.1 g/L, preferably from 0.001 to 0.02 g/L; and, wherein if present, the level of the enzyme in the aqueous solution is from 0.01 to 10ppm, preferably 0.05 to 1ppm.
- 15 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 335 degrees Kelvin.

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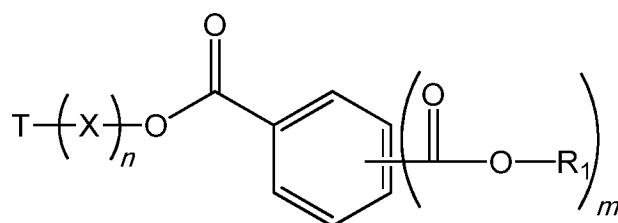
The textile is preferably an item of used clothing, bedding or table cloth. Preferred items of clothing are worn cotton containing shirts, trousers, underwear and jumpers.

### Detailed Description of the Invention

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#### Alkoxyated Dispersant

The alkoxyated dispersant has the following structure:-



wherein:

30

X is selected from: ethoxy; and mixtures of ethoxy and propoxy groups where the number of ethoxy groups is greater than the number of propoxy groups, and wherein  $n$  is from 6 to 70;

- 5  $R_1$  is selected from: uncharged C12 to C20 alkyl groups; uncharged aryl groups; and, uncharged alkyl-aryl groups wherein the alkyl group of the alkyl-aryl is a saturated linear or branched C1 to C3.

Preferably  $R_1$  is an alkyl-aryl group, most preferably benzyl.

- 10 T is selected from: H;  $\text{CH}_3$ ;  $\text{SO}_3^-$ ;  $\text{CH}_2\text{COO}^-$ ;  $\text{PO}_3^{2-}$ ;  $\text{C}_2\text{H}_5$ ; n-propyl, i-propyl; n-butyl; t-butyl; and, sulfosuccinate; preferably T is not H, most preferably T is  $\text{CH}_3$ .  
The value  $m$  is selected from 2 and 3, and is preferably 2.

- The alkoxyated dispersant is preferably formed as a reaction product of trimellitic anhydride or pyromellitic dianhydride with a polyether of the form  $\text{T}-(\text{X})_n-\text{OH}$  and alcohol  
15 of the form  $\text{R}_1-\text{OH}$ , where  $\text{R}_1$  is selected from uncharged C12 to C20 alkyl groups; uncharged aryl groups; and, uncharged alkyl-aryl groups wherein the alkyl group of the alkyl-aryl is a saturated linear or branched C1 to C3.

Preferably  $\text{R}_1-\text{OH}$  is selected from 2-phenylethanol and benzyl alcohol.

20

- $\text{R}_1$  may be substituted by further uncharged organic groups, for example when  $\text{R}_1$  contains a benzene ring the benzene ring may be substituted by methyl, ethyl, methoxy, ethoxy, Cl,  $\text{NO}_2$ . When  $\text{R}_1-\text{OH}$  is an aromatic alcohol, phenol, for example may be used in the reaction. Preferably the trimellitic anhydride or pyromellitic anhydride is reacted  
25 with the polyether then the  $\text{R}_1-\text{OH}$  alcohol. Preferably the trimellitic anhydride or pyromellitic anhydride is reacted with 1 mole equivalent of the polyether then the  $\text{R}_1-\text{OH}$  alcohol.

- X is selected from  $\text{OCH}_2\text{CH}_2$  (ethoxy) and  $\text{OCH}(\text{CH}_3)\text{CH}_2$  (propoxy) and mixtures thereof,  
30 wherein if a mixture, then the number of ethoxy groups is greater than the number of propoxy groups. If X comprises propoxy groups then preferably the mole ratio of ethoxy/propoxy is greater than 2, more preferably greater than 5.

If X is a mixture of ethoxy and propoxy groups, then they may distributed blockwise, alternatively, periodically and/or statistically.

- 35 X is most preferably  $\text{OCH}_2\text{CH}_2$  (ethoxy).

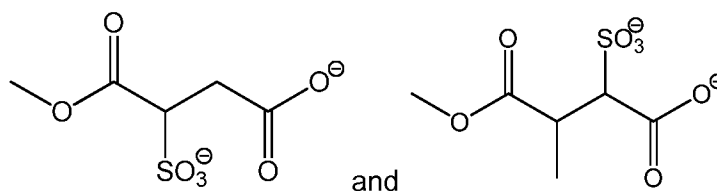
The value  $n$  is the mole average number of alkoxy groups. The value of  $n$  may be measured using NMR. The value of  $n$  is from 6 to 70, preferably 6 to 40, more preferably 9 to 30. Indeed the value of  $n$  may be individually 9, 10, 11, 12, 13, 14; 15; 16; 17; 18; 19; 20; 21; 22; 23; 24; 25; 26; 27; 28; 29, or 30. Most preferably the value of  $n$  may be from 10 to 20.

The alkoxyated dispersant may alternatively be formed by reaction of the anhydride with  $R_1\text{-OH}$  then alkoxylation with an epoxide, however, this route is not preferred.

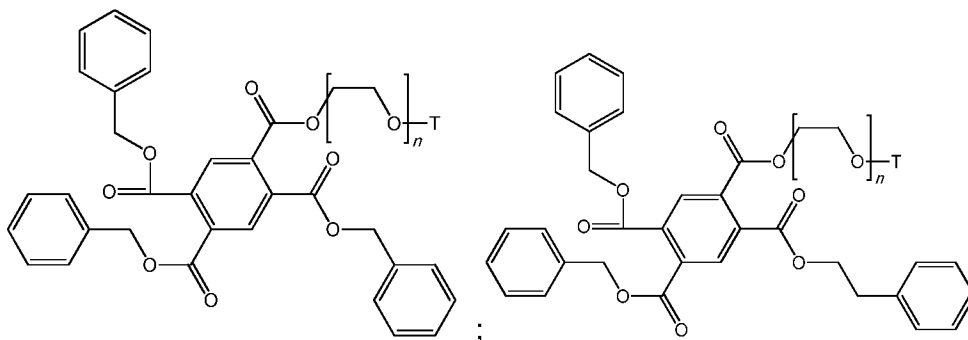
10 Trimellitic anhydride chloride may also be used.

In the context of the current invention the alkoxyated dispersant is not considered a surfactant and does not contribute numerically to the surfactant as defined herein.

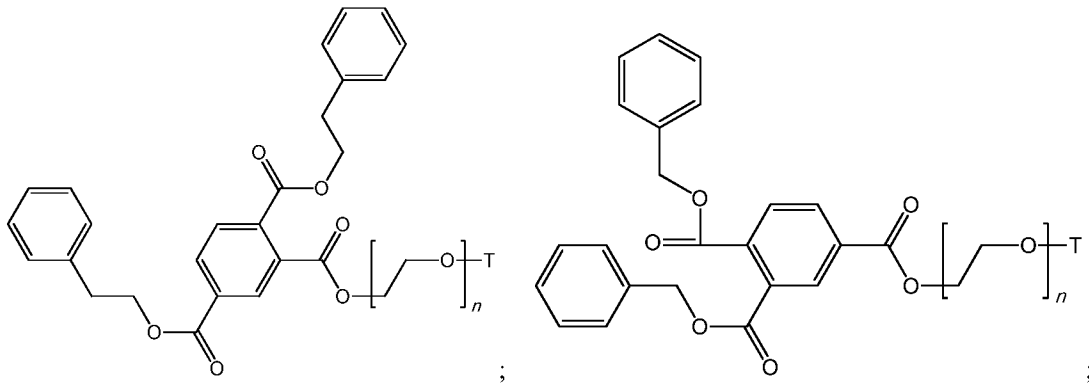
15 Sulfoccinate has the structure:



Preferred examples of structures of the AD of the invention are

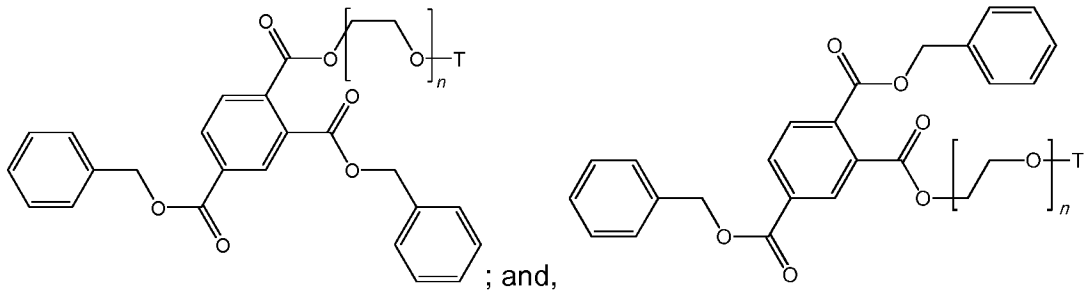






and isomers thereof.

The most preferred AD structures are:



The alkoxydispersant prevents the deposition of soil present in the wash liquor onto the fabric. The alkoxydispersant can also increase stain removal.

10 **Active Ingredient**

The laundry cleaning composition comprises an active ingredient selected from one or more of the following: from 0.001 to 3 wt.% perfume; from 0.0001 to 0.5 wt.% of fluorescent agent; and, from 0.0001 wt.% to 0.1 wt.% of an enzyme.

- 15 Contemplated enzymes include proteases, alpha-amylases, cellulases, lipases, peroxidases/oxidases, pectate lyases, and mannanases, or mixtures thereof.

Preferably the enzyme is selected from: proteases, alpha-amylases; cellulases and lipases, or mixtures thereof. More preferably the enzyme is a protease, more preferably a  
20 subtilase type serine protease.

Preferred perfumes and fluorescent agents are described herein.

**Surfactant**

In the context of the current invention the alkoxyated dispersant is not considered a surfactant and does not contribute numerically to the surfactant as defined herein.

- 5 The laundry composition may comprise anionic and non-ionic surfactant (which includes a mixture of the same).

The surfactant is present at a level of from 0 to 50 wt.%. This means that surfactant need not be present, but it is preferred that it is present.

10

Preferred laundry cleaning compositions comprise surfactant at a level of from 4 to 40 wt.%, more preferably from 4 to 35 wt.%, most preferably from 6 to 30 wt.%.

Preferably the surfactant comprises anionic and/or non-ionic surfactants.

15

Suitable nonionic and anionic surfactants may be chosen from the surfactants described "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

20 "Tenside-Taschenbuch", H. Stache, 2nd Edn., Carl Hauser Verlag, 1981 or in Anionic Surfactants: Organic Chemistry edited by Helmut W. Stache (Marcel Dekker 1996).

Suitable anionic detergent compounds which may be used are usually water-soluble alkali metal salts of organic sulphates and sulphonates having alkyl radicals containing

25 from about 8 to about 22 carbon atoms, the term alkyl being used to include the alkyl portion of higher alkyl radicals.

Examples of suitable synthetic anionic detergent compounds are sodium and potassium alkyl sulphates, especially those obtained by sulphating higher C<sub>8</sub> to C<sub>18</sub> alcohols,

30 produced for example from tallow or coconut oil, Alkyl ether carboxylic acids; sodium and potassium alkyl C<sub>9</sub> to C<sub>20</sub> benzene sulphonates, particularly sodium linear secondary alkyl C<sub>10</sub> to C<sub>15</sub> benzene sulphonates; and sodium alkyl glyceryl ether sulphates, especially those ethers of the higher alcohols derived from tallow or coconut oil and synthetic alcohols derived from petroleum.

35

The anionic surfactant is preferably selected from: linear alkyl benzene sulphonate; alkyl sulphates; alkyl ether sulphates; alkyl ether carboxylates; soaps; alkyl (preferably methyl) ester sulphonates, and mixtures thereof.

- 5 More preferred anionic surfactants are selected from: linear alkyl benzene sulphonate; alkyl sulphates; alkyl ether sulphates and mixtures thereof. Preferably the alkyl ether sulphate is a C<sub>12</sub>-C<sub>14</sub> n-alkyl ether sulphate with an average of 1 to 3EO (ethoxylate) units. Sodium lauryl ether sulphate is particularly preferred (SLES). Preferably the linear alkyl benzene sulphonate is a sodium C<sub>11</sub> to C<sub>15</sub> alkyl benzene sulphonates. Preferably the
- 10 alkyl sulphates is a linear or branched sodium C<sub>12</sub> to C<sub>18</sub> alkyl sulphates. Sodium dodecyl sulphate is particularly preferred, (SDS, also known as primary alkyl sulphate).

Preferably two or more anionic surfactant are present, for example linear alkyl benzene sulphonate together with an alkyl ether sulphate.

15

Most preferably the anionic surfactant is selected from: linear alkyl benzene sulphonates; alkyl sulphates; alkyl ether sulphates; and mixtures thereof.

The composition may comprise anionic and/or non-ionic surfactants.

- 20 Preferably the weight fraction of non-ionic surfactant to anionic surfactant is from 0 to 0.3. This means that non-ionic surfactant can be present (or it may be absent if the weight fraction is 0), but if non-ionic surfactant is present, then the weight fraction of the non-ionic surfactant is preferably at most 30% of the total weight of anionic surfactant + non-ionic surfactant.

25

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. Specific nonionic detergent compounds are

- 30 the condensation products of aliphatic C<sub>8</sub> to C<sub>18</sub> primary or secondary linear or branched alcohols with ethylene oxide.

If a non-ionic surfactant is present, then most preferably the non-ionic surfactant is an alcohol ethoxylate, more preferably a C<sub>10</sub>-C<sub>18</sub> alcohol ethoxylate having an average of 3-

- 10 -

10 moles of ethylene oxide, most preferably an C<sub>12</sub>-C<sub>15</sub> alcohol ethoxylate having an average of 5-9 moles of ethylene oxide.

Preferably the surfactants used are saturated.

5

Also applicable are surfactants such as those described in EP-A-328 177 (Unilever), which show resistance to salting-out, the alkyl polyglycoside surfactants described in EP-A-070 074, and alkyl monoglycosides.

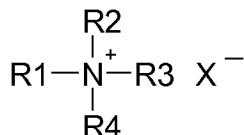
## 10 **Cationic Compound**

The surfactant may comprise a cationic surfactant

Most preferred are quaternary ammonium compounds.

15 It is advantageous if the quaternary ammonium compound is a quaternary ammonium compound having at least one C<sub>12</sub> to C<sub>22</sub> alkyl chain.

It is preferred if the quaternary ammonium compound has the following formula:



20

in which R<sup>1</sup> is a C<sub>12</sub> to C<sub>22</sub> alkyl or alkenyl chain; R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> are independently selected from C<sub>1</sub> to C<sub>4</sub> alkyl chains and X<sup>-</sup> is a compatible anion. A preferred compound of this type is the quaternary ammonium compound cetyl trimethyl quaternary ammonium bromide.

25

A second class of materials for use with the present invention are the quaternary ammonium of the above structure in which R<sup>1</sup> and R<sup>2</sup> are independently selected from C<sub>12</sub> to C<sub>22</sub> alkyl or alkenyl chain; R<sup>3</sup> and R<sup>4</sup> are independently selected from C<sub>1</sub> to C<sub>4</sub> alkyl chains and X<sup>-</sup> is a compatible anion.

30

The composition optionally comprises a silicone.

**Perfume**

One or more perfumes may be present as whole or part of the active ingredient of the laundry cleaning composition.

- 5 The composition preferably comprises a perfume. The perfume is preferably present in the range from 0.001 to 3 wt.%, more preferably 0.05 to 0.5 wt.%, most preferably 0.1 to 1 wt.%. Many suitable examples of perfumes are provided in the CTFA (Cosmetic, Toiletry and Fragrance Association) 1992 International Buyers Guide, published by CFTA Publications and OPD 1993 Chemicals Buyers Directory 80th Annual Edition, published  
10 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;  
15 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; cedryl formate; cyclohexyl salicylate; gamma-dodecalactone; and, beta  
20 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,  
25 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,  
30 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.

5 The International Fragrance Association has published a list of fragrance ingredients (perfums) in 2011, (<http://www.ifraorg.org/en-us/ingredients#.U7Z4hPIdWzk>).

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

10 Perfume top note may be used to cue the 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 (i.e., 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:

20 allyl caproate, amyl acetate, amyl propionate, anisic aldehyde, anisole, benzaldehyde, benzyl acetate, benzyl acetone, benzyl alcohol, benzyl formate, benzyl 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, 25 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 decenyl acetate) , frutene (tricyclco decenyl propionate) , geraniol, hexenol, hexenyl acetate, hexyl acetate, hexyl formate, hydratropic alcohol, hydroxycitronellal, indone, isoamyl 30 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 carbonate, methyl heptyl ketone, methyl hexyl ketone, methyl phenyl carbiny acetate, methyl salicylate, methyl-n-methyl anthranilate, nerol, octalactone, octyl 35 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-terpinenol, and /or viridine. It is commonplace for a plurality of perfume components to be present in a formulation. It is envisaged that there  
5 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.

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,  
10 including components of essential oils such as Clary Sage, Eucalyptus, Geranium, Lavender, Mace Extract, Neroli, Nutmeg, Spearmint, Sweet Violet Leaf and Valerian. It is preferred that the laundry treatment composition does not contain a peroxygen bleach, e.g., sodium percarbonate, sodium perborate, and peracid.

15

### **Fluorescent Agent**

One or more fluorescent agents may be present as whole or part of the active ingredient of the laundry cleaning composition.

20 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.

25 Preferred classes of fluoescer 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.

30 Preferred fluoescers 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.

35

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.%.

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

### **Enzymes**

- 10 Enzymes may be present as whole or part of the active ingredient of the laundry cleaning composition.

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

15

If present, then the level of each enzyme in the laundry composition of the invention is from 0.0001 wt.% to 0.1 wt.%.

- 20 Levels of enzyme present in the composition preferably relate to the level of enzyme as pure protein.

Contemplated enzymes include proteases, alpha-amylases, cellulases, lipases, peroxidases/oxidases, pectate lyases, and mannanases, or mixtures thereof.

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

Suitable lipases include those of bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Examples of useful lipases include lipases from

- 30 *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 95/06720 and  
35 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,  
WO 94/01541, EP 407 225, EP 260 105, WO 95/35381, WO 96/00292,

5 WO 95/30744, WO 94/25578, WO 95/14783, WO 95/22615, WO 97/04079 and  
WO 97/07202, WO 00/60063.

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

10

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 types of phospholipase activity can be distinguished, including

20

phospholipases A<sub>1</sub> and A<sub>2</sub> 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

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 are described in the MEROPS peptidase database

30

(<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

35

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.

5 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 WO 89/06279 and protease PD138 described in (WO  
10 93/18140). Other useful proteases may be those described in WO 92/175177, WO 01/016285, WO 02/026024 and WO 02/016547. Examples of trypsin-like proteases are trypsin (e.g. of porcine or bovine origin) and the Fusarium protease described in WO 89/06270, WO 94/25583 and WO 05/040372, and the chymotrypsin proteases derived from Cellulomonas described in WO 05/052161 and WO 05/052146.

15

Most preferably the protease is a subtilisins (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  
20 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, B. amyloliquefaciens, Bacillus pumilus and Bacillus  
25 gibsonii as described in US 6,312,936 B1, US 5,679,630, US 4,760,025, US7,262,042 and WO 09/021867. Most preferably the subtilisin is derived from Bacillus gibsonii or Bacillus Lentus.

Suitable commercially available protease enzymes include those sold under the trade  
30 names names Alcalase®, Blaze®; Duralase™, Durazym™, Relase®, Relase® 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 Eevity® (Novozymes A/S).

The invention may be use 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.

- 5 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
- 10 Duramyl™, Termamyl™, Termamyl Ultra™, Natalase™, Stainzyme™, Fungamyl™ and BAN™ (Novozymes A/S), Rapidase™ and Purastar™ (from Genencor International Inc.).

- Suitable cellulases include those of bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Suitable cellulases include cellulases from the
- 15 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, 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™,
- 20 Endolase™, Renozyme™ (Novozymes A/S), Clazinase™ and Puradax HA™ (Genencor International Inc.), and KAC-500(B)™ (Kao Corporation). Celluclean™ is preferred.

- Suitable peroxidases/oxidases include those of plant, bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Examples of useful
- 25 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).

- 30 Further enzymes suitable for use are discussed in WO 2009/087524, WO 2009/090576, WO 2009/107091, WO 2009/111258 and WO 2009/148983.

- The aqueous solution used in the method preferably has an enzyme present. The enzyme is preferably present in the aqueous solution used in the method at a
- 35 concentration in the range from 0.01 to 10ppm, preferably 0.05 to 1ppm.

**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.

**Builders or Complexing Agents**

Builder materials may be present. If present then they are generally selected from 1) calcium sequestrant materials, 2) precipitating materials, 3) calcium ion-exchange materials and 4) mixtures thereof.

Examples of calcium sequestrant builder materials include alkali metal polyphosphates, such as sodium tripolyphosphate and organic sequestrants, such as ethylene diamine tetra-acetic acid.

Examples of precipitating builder materials include sodium orthophosphate and sodium carbonate.

Examples of calcium ion-exchange builder materials include the various types of water-insoluble crystalline or amorphous aluminosilicates, of which zeolites are well known representatives, e.g. zeolite A, zeolite B (also known as zeolite P), zeolite C, zeolite X, zeolite Y and also the zeolite P-type as described in EP-A-0,384,070.

The composition may also contain 0-65 % of a builder or complexing agent such as ethylenediaminetetraacetic acid, diethylenetriamine-pentaacetic acid, alkyl- or alkenylsuccinic acid, nitrilotriacetic acid or the other builders mentioned below.

Preferably the laundry cleaning formulation is a non-phosphate built laundry detergent formulation, i.e., contains less than 1 wt.% of phosphate.

The laundry cleaning formulation is most preferably an aqueous liquid laundry detergent.

In the aqueous liquid laundry detergent it is preferred that mono propylene glycol is present at a level from 1 to 30 wt.%, most preferably 2 to 18 wt.%.

### **Polymers**

- 5 The composition may preferably comprise one or more polymers. Example polymers are carboxymethylcellulose, poly(ethylene glycol), poly(vinyl alcohol), polycarboxylates such as polyacrylates, maleic/acrylic acid copolymers and lauryl methacrylate/acrylic acid copolymers.
- 10 Polymers present to prevent dye deposition may be present, for example poly(vinylpyrrolidone), poly(vinylpyridine-N-oxide), and poly(vinylimidazole).

### **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).
- 15

- Shading Dyes for use in laundry compositions preferably have an extinction coefficient at the maximum absorption in the visible range (400 to 700nm) of greater than
- 20 5000 L mol<sup>-1</sup> cm<sup>-1</sup>, preferably greater than 10000 L mol<sup>-1</sup> cm<sup>-1</sup>. The dyes are blue or violet in colour.

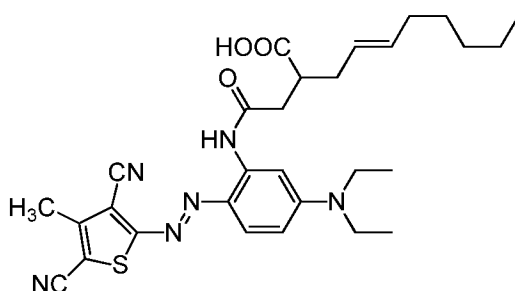
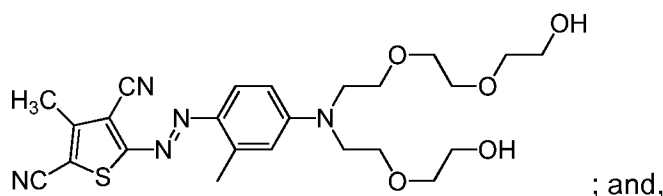
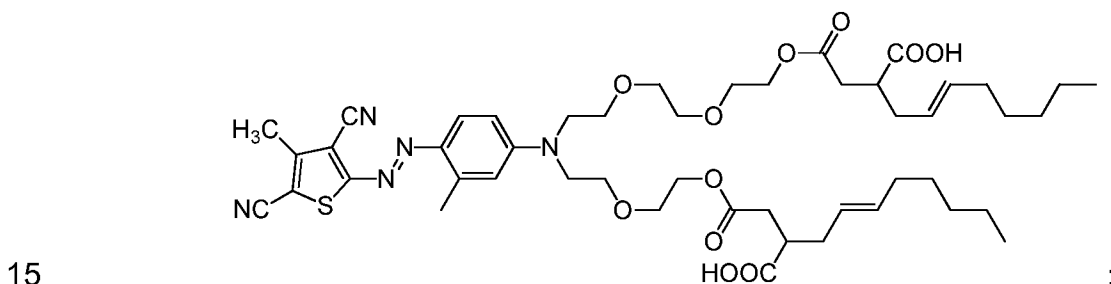
- Preferably the composition comprises a shading dye. Preferably the shading dye is present at from 0.0001 to 0.1 wt.% of the composition.

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

- Azo, anthraquinone, phthalocyanine and triphenylmethane dyes preferably carry a net anionic charged or are uncharged. Azine preferably carry a net anionic or cationic charge. Blue or violet shading dyes deposit to fabric during the wash or rinse step of the washing process providing a visible hue to the fabric. In this regard the dye gives a blue or violet colour to a white cloth with a hue angle of 240 to 345, more preferably 250 to 320, most preferably 250 to 280. The white cloth used in this test is bleached non-
- 35 mercerised woven cotton sheeting.

Shading dyes are discussed in WO 2005/003274, WO 2006/032327(Unilever),  
 WO 2006/032397(Unilever), WO 2006/045275(Unilever), WO 2006/027086(Unilever),  
 WO 2008/017570(Unilever), WO 2008/141880 (Unilever), WO 2009/132870(Unilever),  
 5 WO 2009/141173 (Unilever), WO 2010/099997(Unilever), WO 2010/102861(Unilever),  
 WO 2010/148624(Unilever), WO 2008/087497 (P&G), WO 2011/011799 (P&G), WO  
 2012/054820 (P&G), WO 2013/142495 (P&G) and WO 2013/151970 (P&G).

Mono-azo dyes preferably contain a heterocyclic ring and are most preferably thiophene  
 10 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:

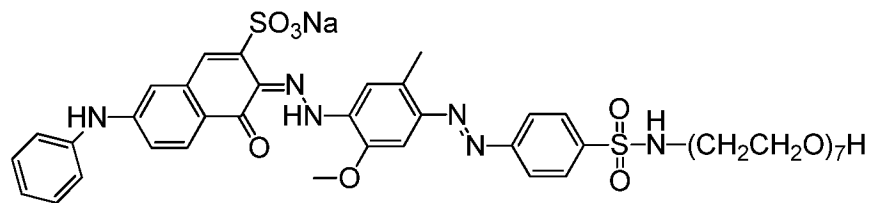


20

Bis-azo dyes are preferably sulphonated bis-azo dyes. Preferred examples of  
 sulphonated bis-azo compounds are direct violet 7, direct violet 9, direct violet 11,

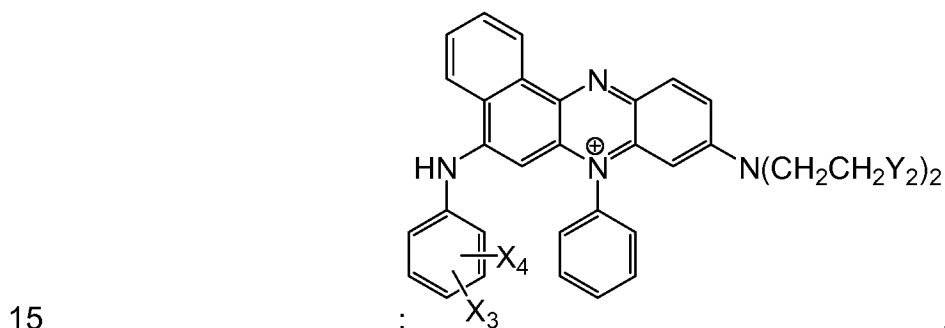
direct violet 26, direct violet 31, direct violet 35, direct violet 40, direct violet 41, direct violet 51, Direct Violet 66, direct violet 99 and alkoxyated versions thereof. Alkoxyated bis-azo dyes are discussed in WO2012/054058 and WO2010/151906.

5 An example of an alkoxyated bis-azo dye is :



10 Thiophene dyes are available from Milliken under the tradenames of Liquitint Violet DD and Liquitint Violet ION.

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, and the phenazine dye selected from:



wherein:

$X_3$  is selected from: -H; -F; -CH<sub>3</sub>; -C<sub>2</sub>H<sub>5</sub>; -OCH<sub>3</sub>; and, -OC<sub>2</sub>H<sub>5</sub>;

$X_4$  is selected from: -H; -CH<sub>3</sub>; -C<sub>2</sub>H<sub>5</sub>; -OCH<sub>3</sub>; and, -OC<sub>2</sub>H<sub>5</sub>;

20  $Y_2$  is selected from: -OH; -OCH<sub>2</sub>CH<sub>2</sub>OH; -CH(OH)CH<sub>2</sub>OH; -OC(O)CH<sub>3</sub>; and, C(O)OCH<sub>3</sub>.

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.

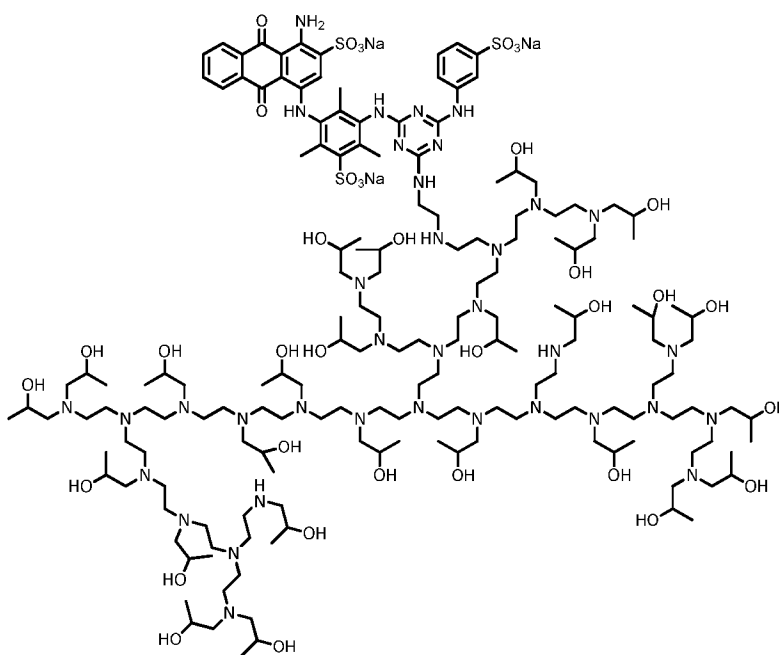
5

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).

20

### **Misc**

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.



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.

### **Experimental**

- 5 The examples below are intended to illustrate the invention in detail without, however, limiting it thereto.

### **Synthesis**

- 10 Trimellitic acid was used as purchased from ACROS Organics. Trimellitic anhydride and pyromellitic acid was used as purchased from Alfa Aesar. Phenoxyethanol, para-toluene sulfonic acid and titanium isopropoxide were used as purchased from Merck.

Methanesulfonic acid, 4-dodecylbenzenesulfonic acid mixture of isomers and benzyl alcohol were used as purchased from Sigma Aldrich.

- 15 Lauryl/myristyl alcohol and cetearyl alcohol were used in technical grade quality and their molecular masses were determined prior to use by measuring the hydroxyl value (OH-value) and subsequently calculating the molecular weight (per hydroxyl function, “Gebrauchsmol”). In this case the OH-value may be measured according to DIN 53240.

- 20 The acid number (acid value) may be measured according to DIN EN ISO 2114.

Polyglykols M are mono hydroxy-functional polyethylene glycol monomethyl ethers (M-PEG, CAS-Nr. 9004-74-4).

- 25 Polyglykol M 500 is a linear, mono hydroxy-functional polyethylene glycol monomethyl ether (M-PEG) that has a molecular weight of 470-530 g/mol.

Polyglykol M 750 is a linear, mono hydroxy-functional polyethylene glycol monomethyl ether (M-PEG) that has a molecular weight of 720-780 g/mol.

30

Polyglykol M 1000 is a linear, mono hydroxy-functional polyethylene glycol monomethyl ether (M-PEG) that has a molecular weight of 970 - 1060 g/mol.

- 35 Polyglykol M 1250 is a linear, mono hydroxy-functional polyethylene glycol monomethyl ether (M-PEG) that has a molecular weight of 1125-1375 g/mol.

Polyglykol M 2000 is a linear, mono hydroxy-functional polyethylene glycol monomethyl ether (M-PEG) that has a molecular weight of 1800 - 2200 g/mol.

5 The degree of alkoxylation of the used methyl polyglykols may be checked using NMR spectroscopy, for example using <sup>1</sup>H-NMR spectroscopy in analogy to the method described in R. Stevanova, D. Rankoff, S. Panayotova, S.L. Spassov, J. Am. Oil Chem. Soc., 65, 1516-1518 (1988). For this purpose, the samples are derivatised by reacting them with trichloro acetyl isocyanate and measured as solutions in deuterated chloroform containing 1 weight-% (1 wt.-%) of tetramethyl silane as an internal standard.

10

The esterification reactions were controlled by determining the residual content of alcohol (e.g. benzyl alcohol, phenoxyethanol, lauryl myristyl alcohol and cetearyl alcohol) by GC-FID. Calibration was performed with pure starting materials. Gas chromatography (GC) was performed using a Hewlett Packard GC 6890 with autosampler, coupled with a  
15 flame-ionisation detector (FID).

20

For the quantification of benzyl alcohol, samples were separated on a 50 m x 0.2 mm, 0.33 µm film column. The column temperature was initially held at 50°C, then the temperature was raised to 175°C at a rate of 5°C per minute and from 175°C to 300°C at  
a rate of 25°C per minute. The injector temperature was maintained at 250°C and the injection volume was 1.0 µL in the split mode. Helium was used as a carrier gas with a constant pressure of 1.8 bar. The samples were prepared by diluting 500 mg of sample (duplicate analysis) with 5 ml of methanol.

25

For the quantification of phenoxyethanol, cetearyl alcohol and dodecanol, samples were separated on a 25 m x 0.32 mm, 0.52 µm film column. The column temperature was initially held at 50°C, then the temperature was raised to 250°C at a rate of 10°C per minute and held for 6.5 minutes. The injector temperature was maintained at 250°C and the injection volume was 1.0 µL in the split mode. Helium was used as a carrier gas with  
30 a constant pressure of 0.9 bar. The samples were prepared by diluting 500 mg of sample (duplicate analysis) with 5 ml of methanol.

35

Thin layer chromatography (TLC) was performed using TLC Silica Gel 60 F254 plates from Merck. The aromatic compounds were detected by UV light (254 and 366 nm simultaneously).

All examples, unless otherwise stated, were performed according to a standard procedure. All reagents and quantities are listed in Table I.

5 The alcohol alkoxylate of choice was heated to 80°C with stirring under nitrogen. The polycarboxylic acid or acid anhydride of choice was then added in portions over 5 minutes. The reaction mixture was then stirred for 2.5 hours at 80°C. The product, henceforth termed precursor, was isolated and the acid number determined – these are listed in Table I in the column AN1.

10 Some amount of the precursor (listed in the column “PC” of Table I) was mixed with the alcohol and catalyst of choice and heated to the temperature listed in Table I while stirring under nitrogen. The reaction mixture was stirred at the temperature listed for the time denoted in Table I and water was distilled off. For all examples except examples 1, 2, 10 and 11, the product was then isolated after cooling and the acid number of the final  
15 product determined – listed as AN2 in Table I.

In the cases of examples 10 and 11, a vacuum of 500 mbar was applied at 180°C for 3 h under stirring after completion of stirring for the time listed in Table I.

20 The abbreviations used in Table I are as follows:

|          |                                  |
|----------|----------------------------------|
| AA       | alcohol alkoxylate               |
| PCA      | polycarboxylic acid              |
| PC       | precursor                        |
| BA       | benzyl alcohol                   |
| 25 PE    | phenoxyethanol                   |
| C16/18   | cetearyl alcohol                 |
| AN1      | acid number of the precursor     |
| AN2      | acid number of the final product |
| M750     | Polyglykol M 750                 |
| 30 M1250 | Polyglykol M 1250                |
| TMAA     | trimellitic acid anhydride       |
| pTsOH    | p-toluene sulfonic acid          |

**Table I: Example Dispersant Compositions**

|                               | <b>1</b>      | <b>2</b>        | <b>3</b>        | <b>4</b>      | <b>C1</b>      |
|-------------------------------|---------------|-----------------|-----------------|---------------|----------------|
| AA (g)                        | M750<br>450.0 | M1250<br>1300.0 | M1250<br>2800.0 | M750<br>806.4 | M750<br>1000.0 |
| PCA (g)                       | TMAA<br>115.3 | TMAA<br>199.8   | TMAA<br>430.4   | TMAA<br>213.0 | TMAA<br>256.2  |
| PC (g)                        | 130           | 400             | 400             | 320           | -              |
| BA (g)                        | 37.7          | -               | -               | -             | -              |
| PE (g)                        | -             | 95.8            | -               | 120.1         | -              |
| C16/C18 (g)                   | -             | -               | 146.1           | -             | -              |
| Cat (g)                       | pTsOH<br>0.17 | pTsOH<br>0.50   | pTsOH<br>0.55   | pTsOH<br>0.44 | -              |
| Temp (°C)                     | 200           | 180             | 180             | 180           | 80             |
| Time (hr)                     | 44.5          | 40              | 41              | 43            | 2.5            |
| AN1<br>(mg KOH per<br>g)      | 130.6         | 80.0            | 79.0            | 121.9         | 120.0          |
| AN2<br>(mg KOH per<br>g)      | 23.4          | 18.8            | 15.6            | 17.3          | -              |
| Residual<br>Alcohol<br>(wt.%) | 1.1           | 1.3             | 8.7             | 1.1           | -              |

- 5 As a comparative example, sample C1 from Table I was isolated after the first synthesis step and no reaction with alcohol was performed.

An aqueous liquid laundry detergent of the following formulation was prepared:

**Table II: Liquid laundry detergent formulation**

| <b>Ingredient</b>  | <b>weight-%</b> |
|--|-----------------|
| Mono propylene glycol  | 2.2             |
| Triethanolamine  | 1.5             |
| C <sub>12</sub> -C <sub>15</sub> alcohol ethoxylate with 7 moles of ethylene oxide | 1.2             |
| Linear alkyl benzene sulfonate   | 4.6             |
| Sodium laureth ether sulphate with 1 moles of ethylene oxide                       | 5.8             |
| Citric acid  | 2.0             |
| CaCl <sub>2</sub> dihydrate  | 0.2             |
| NaCl   | 0.2             |
| Tinopal® CBS-X (fluorescer BASF)   | 0.3             |
| Sodium Hydroxide   | to pH = 8.4     |
| Exemplary dispersants  | see text        |
| Water  | balance         |

Application Example 1 – Anti-Redeposition Benefit

The formulation was used to wash eight 5x5 cm knitted cotton cloth pieces in a Tergotometer set at 200 rpm (revolutions per minute). A one hour wash was conducted in 800 ml of water with 26° French hardness at 20°C, with 2.3 g/l of the formulation shown in Table II. To simulate particulate soil that could redeposit, 0.04 g/l of 100% compressed carbon black (ex Alfa Aesar) was added to the wash liquor. To simulate oily sebaceous soil, 7.2 g of an SBL2004 soil strip (ex Warwick Equest) was added to the wash liquor.

Once the wash had been completed, the cotton swatches were rinsed once in 400 ml clean water, removed, dried and the colour measured on a reflectometer and expressed as the CIE L\*a\*b\* values. The anti-redeposition benefit was expressed as the  $\Delta L$  value:

$$\Delta L = L^*(\text{dispersant}) - L^*(\text{control})$$

The larger the  $\Delta L$  value, the greater the prevention of deposition of the carbon black soil. 95% confidence limits based on the 8 separate cotton swatches were calculated.

Formulations were made with and without the addition of 8.7 wt.-% of the dispersants of Table I. The results are given in Table III.

**Table III: Anti-redeposition benefit**

| <b>Exemplary dispersant</b> | <b><math>\Delta L</math></b> | <b>95 %</b> |
|-----------------------------|------------------------------|-------------|
| Example 1                   | 4.4                          | 0.3         |
| Example 2                   | 2.5                          | 0.3         |
| Example 3                   | 2.5                          | 0.3         |
| Example 4                   | 3.1                          | 0.2         |
| Example C1 (reference)      | 0.5                          | 0.3         |

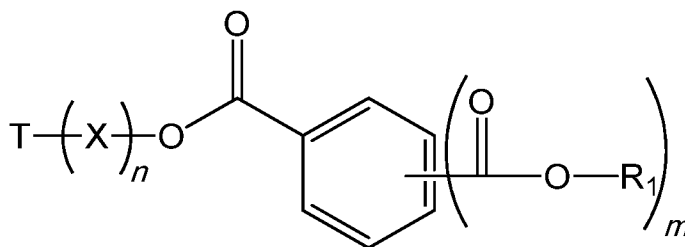
5

The inventive dispersants enhance anti-redeposition.

**CLAIMS**

1. A laundry cleaning composition comprising:

- 5 (i) from 0.2 to 20 wt.%, preferably 0.5 to 12 wt.%, more preferably 1 to 10 wt.% of an alkoxyated dispersant of the following structure:



wherein:

10

X is selected from: ethoxy; and mixtures of ethoxy and propoxy groups, wherein the number of ethoxy groups is greater than the number of propoxy groups, and wherein  $n$  is from 6 to 70;

$m$  is selected from: 2 and 3;

15

$R_1$  is selected from: uncharged C12 to C20 alkyl groups; uncharged aryl groups; and, uncharged alkyl-aryl groups wherein the alkyl group of the alkyl-aryl is a saturated linear or branched C1 to C3;

T is selected from: H; CH<sub>3</sub>; SO<sub>3</sub><sup>-</sup>; CH<sub>2</sub>COO<sup>-</sup>; PO<sub>3</sub><sup>2-</sup>; C<sub>2</sub>H<sub>5</sub>; n-propyl, i-propyl; n-butyl; t-butyl; and, sulfosuccinate;

20

(ii) from 0 to 50 wt.% surfactant, other than the alkoxyated dispersant; and

(iii) an active ingredient selected from one or more of the following: from 0.001 to 3 wt.% perfume; from 0.0001 to 0.5 wt.% of fluorescent agent; and, from 0.0001 wt.% to 0.1 wt.% of an enzyme.

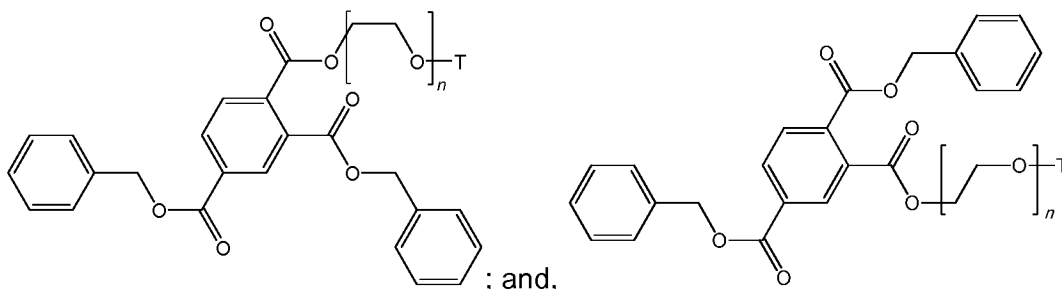
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2. A laundry cleaning composition according to claim 1, wherein  $R_1$  is an alkyl-aryl group.

30

3. A laundry cleaning composition according to claim 1 or 2, wherein T is not H.

4. A laundry cleaning composition according to any preceding claim, wherein X is ethoxy.
5. A laundry cleaning composition according to any one of the preceding claims, wherein  $n$  is from 6 to 40, preferably from 9 to 30, more preferably from 10 to 20.
6. A laundry cleaning composition according to any one of the preceding claims, wherein T is CH<sub>3</sub>.
7. A laundry cleaning composition according to any one of the preceding claims, wherein R<sub>1</sub> is selected from: phenylethyl and benzyl, preferably R<sub>1</sub> is benzyl.
8. A laundry cleaning composition according to any preceding claim, wherein the alkoxyated dispersant is selected from:



9. A laundry cleaning composition according to any one of the preceding claims, wherein the surfactant is present at a level of from 4 to 40 wt.%, preferably from 4 to 35 wt.%, more preferably from 6 to 30 wt.%, and the surfactant comprises anionic and/or non-ionic surfactants, preferably wherein the weight fraction of non-ionic surfactant to anionic surfactant is from 0 to 0.3, wherein the alkoxyated dispersant is not considered a surfactant as defined herein.
10. A laundry cleaning composition according to claim 9, wherein the anionic surfactant is selected from: linear alkyl benzene sulphonates; alkyl sulphates; alkyl ether sulphates; and mixtures thereof.
11. A laundry cleaning composition according to claim 9 or claim 10, comprising a non-ionic surfactant, wherein the non-ionic surfactant is an alcohol ethoxylate, preferably an C<sub>10</sub>-C<sub>18</sub> alcohol ethoxylate having an average of 3-10 moles of



ethylene oxide, more preferably an C<sub>12</sub>-C<sub>15</sub> alcohol ethoxylate having an average of 5-9 moles of ethylene oxide.

12. A laundry cleaning composition according to any one of the preceding claims,  
5 wherein the composition is an aqueous liquid detergent composition having a pH from 6 to 8.5, preferably from 6.5 to 7.5, more preferably from 6.8 to 7.2, most preferably 7.0.
13. A laundry cleaning composition according to any preceding claim, wherein the  
10 active ingredient is an enzyme and comprises one or more of the following: proteases, alpha-amylases, cellulases, lipases, peroxidases/oxidases, pectate lyases, and mannanases, or mixtures thereof, preferably the enzyme is a protease, more preferably a subtilase type serine protease.
14. A domestic method of treating a textile, the method comprising the steps of:  
15
- (i) treating a textile with an aqueous solution of the alkoxyated dispersant as defined in any one of claims 1 to 8;  
20 the aqueous solution comprising from 10 ppm to 5000 ppm, preferably from 100 ppm to 1000 ppm of the alkoxyated dispersant; and, from 0 to 6 g/L, preferably from 0.5 to 6 g/L, more preferably from 1 to 5 g/L of a surfactant, other than the alkoxyated dispersant; and,
- (ii) optionally rinsing and drying the textile;  
25 wherein in the method one or more of an active ingredient selected from perfume, fluorescent agent and enzyme is present in the aqueous solution of the alkoxyated dispersant, wherein if present, the level of the perfume in the aqueous solution is from 0.1 to 100 ppm;  
30 wherein if present, the level of the fluorescent agent in the aqueous solution is from 0.0001 g/l to 0.1 g/L, preferably from 0.001 to 0.02 g/L; and, wherein if present, the level of the enzyme in the aqueous solution is from 0.01 to 10ppm, preferably 0.05 to 1ppm.

**INTERNATIONAL SEARCH REPORT**

International application No  
PCT/EP2018/068090

|   |          |          |          |           |
|---|----------|----------|----------|-----------|
| <b>A. CLASSIFICATION OF SUBJECT MATTER</b>  |          |          |          |           |
| INV. C11D1/37   | C11D1/83 | C11D3/00 | C11D3/37 | C11D3/386 |
|   | C11D3/42 | C11D3/50 |          |           |
| ADD. C11D1/06   | C11D1/29 | C11D1/34 | C11D1/74 |           |
| According to International Patent Classification (IPC) or to both national classification and IPC |          |          |          |           |

|   |
|---|
| <b>B. FIELDS SEARCHED</b>   |
| Minimum documentation searched (classification system followed by classification symbols)<br>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, CHEM ABS Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages  | Relevant to claim No. |
|-----------|---|-----------------------|
| X         | WO 2016/041670 A1 (UNILEVER PLC [GB]; UNILEVER NV [NL]; CONOPCO INC DBA UNILEVER [US]) 24 March 2016 (2016-03-24) page 1, line 33 - page 2, line 12 examples claims | 1-14                  |
| X         | EP 0 035 478 A1 (EKA AB [SE]) 9 September 1981 (1981-09-09) page 1, lines 1-4 page 3, lines 5-30 page 4, lines 4-27 examples claims                                 | 1-14                  |
|           | -----<br>-/--   |                       |

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  |
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| "O" document referring to an oral disclosure, use, exhibition or other means  |  |
| "P" document published prior to the international filing date but later than the priority date claimed  | "&" document member of the same patent family  |

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| Date of the actual completion of the international search<br><br>17 September 2018 | Date of mailing of the international search report<br><br>24/09/2018 |
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| Name and mailing address of the ISA/<br>European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040,<br>Fax: (+31-70) 340-3016 | Authorized officer<br><br>Bertran Nadal, Josep |
|--|--|

## INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2018/068090

| C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT |  |                       |
|--|--|-----------------------|
| Category*  | Citation of document, with indication, where appropriate, of the relevant passages   | Relevant to claim No. |
| A  | WO 2016/041678 A1 (UNILEVER PLC [GB];<br>UNILEVER NV [NL]; CONOPCO INC DBA UNILEVER<br>[US]) 24 March 2016 (2016-03-24)<br>page 1, line 33 - page 2, line 12<br>examples<br>claims | 1-14                  |
| A  | -----<br>US 2015/218491 A1 (MORSCHHAEUSER ROMAN<br>[DE] ET AL) 6 August 2015 (2015-08-06)<br>paragraphs [0006] - [0012], [0025] -<br>[0029]  | 1-14                  |
| A  | -----<br>US 2002/160924 A1 (BERTREM JAN [BE] ET AL)<br>31 October 2002 (2002-10-31)<br>paragraphs [0008], [0083]<br>-----  | 1-14                  |

# INTERNATIONAL SEARCH REPORT

Information on patent family members

|   |
|---|
| International application No<br>PCT/EP2018/068090 |
|---|

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date  |
|--|------------------|-------------------------|---|
| WO 2016041670                          | A1               | 24-03-2016              | AR 101876 A1 18-01-2017<br>AU 2015317265 A1 16-02-2017<br>BR 112017004978 A2 23-01-2018<br>CL 2017000325 A1 18-08-2017<br>CN 107075412 A 18-08-2017<br>EP 3194542 A1 26-07-2017<br>WO 2016041670 A1 24-03-2016      |
| EP 0035478                             | A1               | 09-09-1981              | EP 0035478 A1 09-09-1981<br>JP S56129299 A 09-10-1981   |
| WO 2016041678                          | A1               | 24-03-2016              | AR 101880 A1 18-01-2017<br>BR 112017005154 A2 24-04-2018<br>CN 107075416 A 18-08-2017<br>EP 3194547 A1 26-07-2017<br>WO 2016041678 A1 24-03-2016  |
| US 2015218491                          | A1               | 06-08-2015              | BR 112015003066 A2 04-07-2017<br>CN 104704103 A 10-06-2015<br>DE 102012016462 A1 20-02-2014<br>EP 2885390 A1 24-06-2015<br>JP 2015532664 A 12-11-2015<br>US 2015218491 A1 06-08-2015<br>WO 2014029479 A1 27-02-2014 |
| US 2002160924                          | A1               | 31-10-2002              | NONE  |