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(54) **Title**: WHITENING COMPOSITION

(57) **Abstract**: The present invention provides a domestic laundry cleaning composition.



WO 2017/140392 A1

WHITENING COMPOSITION

Field of Invention

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The present invention concerns the use of cleaning laundry compositions.

Background of the Invention

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Maintaining and improving the cleaning of textiles during domestic laundry is desirable.

Protease enzymes are used in laundry detergent formulations to remove protein containing stains from fabrics. Protease enzyme do not perform well at low temperatures and with short wash times.

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There is a need to increase stain removal in laundry formulations containing protease enzymes for low temperature quick washes.

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Summary of the Invention

There is a need for technologies to increase stain removal in laundry formulations containing protease enzymes.

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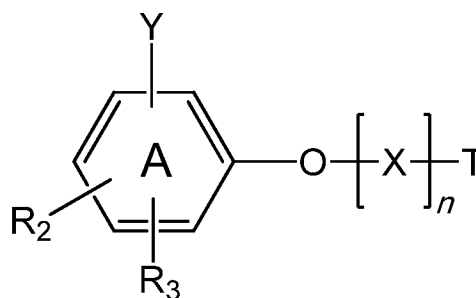
We have found that selected alkoxyated substituted phenol (ASP) dispersants when incorporated into laundry detergents with a protease enzyme increase stain removal.

In one aspect the present invention provides a laundry detergent composition comprising:

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- (i) from 0.5 to 20 wt%, preferably 1 to 10 wt%, most preferably 2 to 6 wt%, of an alkoxyated substituted phenol dispersant of the following structure:

- 2 -



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, preferably from 8 to 34; most preferably n is selected from 14; 15; 16; 17; 18; 19; 20; 21; 22; 23; 24; 25; 26; 27; 28; 29; 30; 31; and, 32;

preferably X is ethoxy;

Y is selected from: R_1 ; OR_1 ; $COOR_5$; F; Cl; Br; I; CN; and NO_2 , wherein R_1 is a C1 to C4 linear or branched alkyl group and wherein R_5 is a C1 to C18 linear or branched alkyl group, preferably R_5 is a C1 to C4 linear or branched alkyl group, most preferably R_5 is methyl; preferably Y is selected from methyl, ethyl, methoxy, ethoxy, most preferably methoxy or methyl;

R_2 and R_3 are selected from: C1 to C3 linear or branched alkyl aryl groups; and, aryl groups; preferably R_2 and R_3 are selected from styryl and cumyl, most preferably styryl, preferably both R_2 and R_3 are in the ortho position to the $-O-[X]_n-T$ group;

T is selected from: H; CH_3 ; SO_3^- ; CH_2COO^- ; PO_3^{2-} ; C_2H_5 ; n-propyl, i-propyl; n-butyl; t-butyl; and, sulfosuccinate, T is preferably H;

- (ii) from 0 to 50 wt% surfactant, other than the alkoxyated substituted phenol dispersant; preferably the surfactant is selected from: anionic and non-ionic surfactants, preferably the level of surfactant is from 4 to 40 wt%, more preferably 6 to 30 wt%, most preferably 8 to 20 wt%; preferably the weight fraction of non-ionic surfactant/anionic surfactant is from 0 to 0.3, preferably 0 to 0.15, most preferably 0.05 to 0.12; and,

(iii) from 0.0005 to 0.2 wt% of a protease enzyme, preferably from 0.002 to 0.05 wt %.

The level of a protease enzyme in the laundry composition of the invention is the level of pure protein.

5

Preferably the composition additionally comprises from 0.0001 to 0.5 wt % of a fluorescent agent and/or from 0.0001 wt% to 0.1 wt% shading dye.

10 The laundry detergent composition is preferably selected from a granular detergent powder; and an aqueous laundry liquid detergent; most preferably the laundry detergent composition is an aqueous laundry liquid detergent composition.

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

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(i) treating a textile with an aqueous solution of the alkoxylated substituted phenol dispersant the aqueous solution comprising from 10 ppm to 5000 ppm, more preferably from 100 ppm to 1000ppm, of the alkoxylated substituted phenol dispersant as defined herein; from 0.01 to 1ppm of a protease enzyme and, 0 to 6
20 g/L of a surfactant, preferably 0.2 to 1 g/L, other than the alkoxylated substituted phenol dispersant; and,

(ii) optionally rinsing and drying the textile.

25 In the method the level of the protease in the aqueous solution is more preferably from 0.02 to 0.2 ppm.

In the method the surfactant is of the type as preferred herein.

30 In the method the level of the perfume in the aqueous solution is preferably from 0.1 to 100 ppm, more preferably from 1 to 10 ppm.

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

35

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.

- 5 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

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Alkoxylated Substituted Phenol

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In the context of the current invention the alkoxylated substituted phenol (ASP) is not considered a surfactant and does not contribute numerically to the surfactant as defined herein.

The most preferred aryl groups are phenyl and substituted phenyl.

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C1 to C3 linear or branched alkyl aryl groups are C1 to C3 linear or branched alkyl groups substituted by an aromatic group, for example: styryl, cumyl, benzyl.

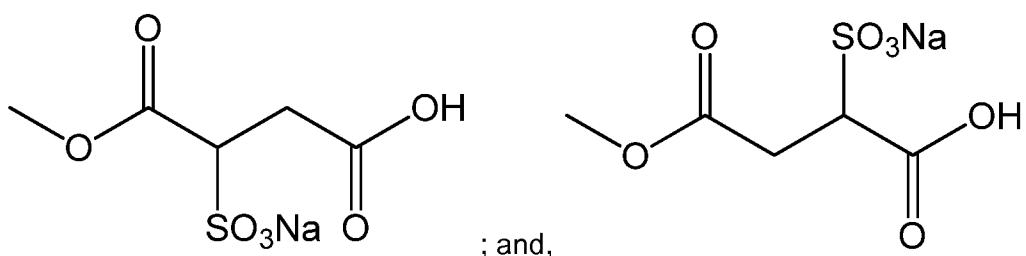
A styryl group is $-\text{CH}(\text{CH}_3)\text{Ph}$; a cumyl group is $-\text{C}(\text{CH}_3)_2\text{Ph}$; a benzyl group is CH_2Ph , where Ph is phenyl.

25

The value n is the mole average number of alkoxy groups. The value of n may be measured using NMR.

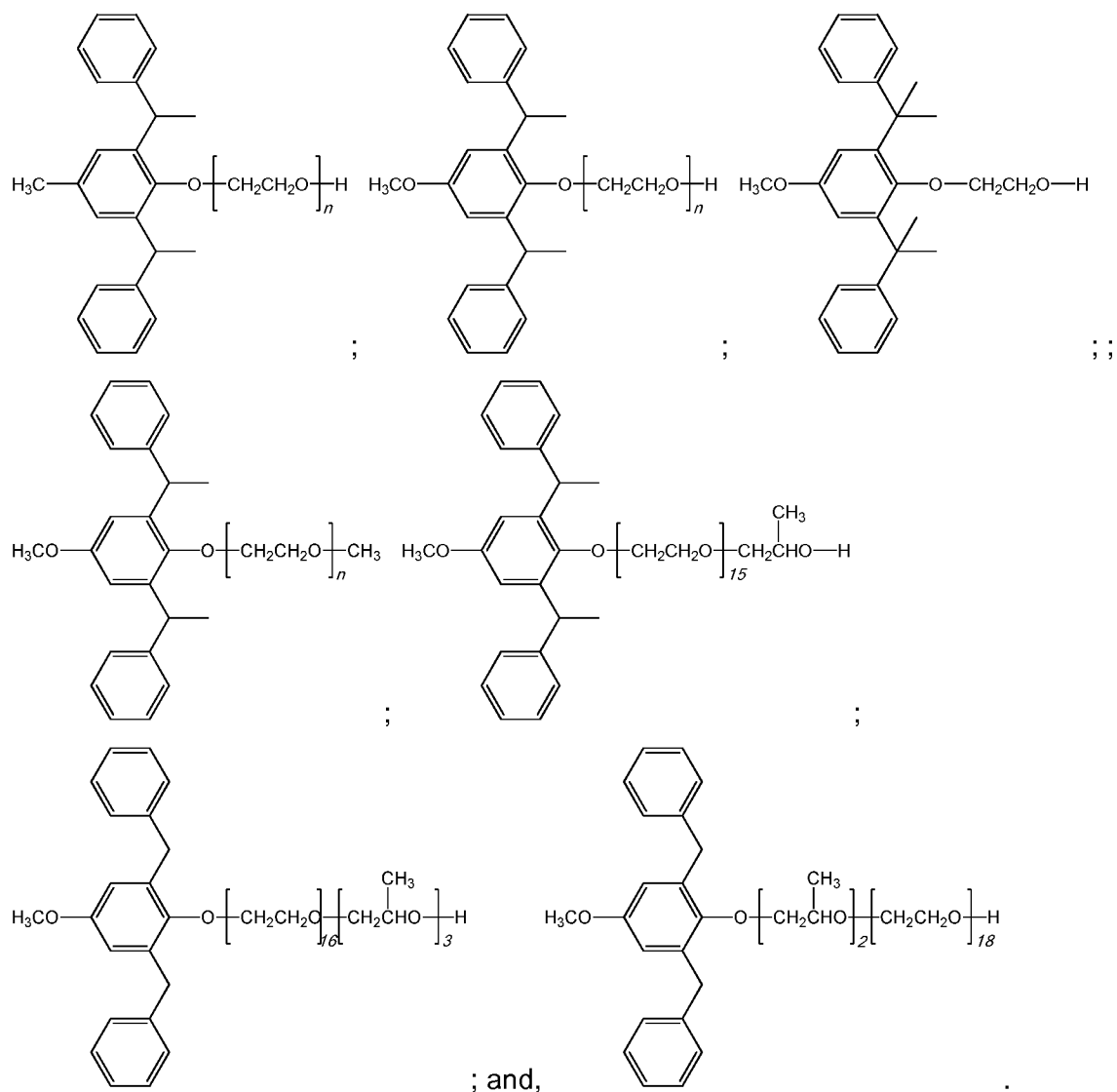
Sulfocinate has the structure, depicted as the Na salt:

30



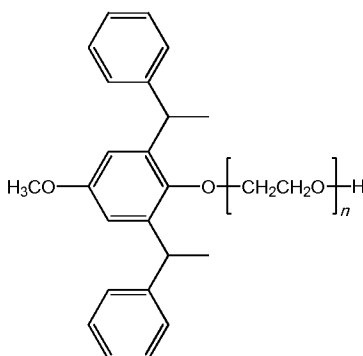
- 5 -

Example of structures of the ASP of the invention are:



The most preferred ASP structure is

- 6 -



5 The ASP in combination with the protease enzyme enhance stain removal and reduces the redeposition of soils, both of which enhance the whiteness of fabrics.

Surfactant

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

The nonionic and anionic surfactants of the surfactant system 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
 15 "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) .

20 Suitable anionic detergent compounds which may be used are usually water-soluble alkali metal salts of organic sulphates and sulphonates having alkyl radicals containing from about 8 to about 22 carbon atoms, the term alkyl being used to include the alkyl portion of higher alkyl radicals.

25 Examples of suitable synthetic anionic detergent compounds are sodium and potassium alkyl sulphates, especially those obtained by sulphating higher C₈ to C₁₈ alcohols, produced for example from tallow or coconut oil, sodium and potassium alkyl C₉ to C₂₀ benzene sulphonates, particularly sodium linear secondary alkyl C₁₀ to C₁₅ 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.

- 5 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.

- The most preferred anionic surfactants are selected from: linear alkyl benzene
10 sulphonate; alkyl sulphates; alkyl ether sulphates and mixtures thereof. Preferably the alkyl ether sulphate is a C₁₂-C₁₄ 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 C₁₁ to C₁₅ alkyl benzene sulphonates. Preferably the alkyl sulphates is a linear or branched sodium C₁₂ to C₁₈
15 alkyl sulphates. Sodium dodecyl sulphate is particularly preferred, (SDS, also known as primary alkyl sulphate).

- The level of anionic surfactant in the laundry composition is preferably from 4 to 40 wt%, more preferably 6 to 30 wt%, and most preferably 8 to 20 wt%.
20 Preferably two or more anionic surfactant are present, for example linear alkyl benzene sulphonate together with an alkyl ether sulphate.

- Preferably the laundry composition in addition to the anionic surfactant comprises alkyl
25 ethoxylated non-ionic surfactant.

- 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
30 oxide either alone or with propylene oxide. Specific nonionic detergent compounds are the condensation products of aliphatic C₈ to C₁₈ primary or secondary linear or branched alcohols with ethylene oxide.

- Preferably the alkyl ethoxylated non-ionic surfactant is a C₈ to C₁₈ primary alcohol with an
35 average ethoxylation of 7EO to 9EO units.

Preferably the surfactants used are saturated.

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
5 EP-A-070 074, and alkyl monoglycosides.

Builders or Complexing Agents

Builder materials may be selected from 1) calcium sequestrant materials, 2) precipitating
10 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.
15

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.
20

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. Many builders are also bleach-stabilising agents by virtue of their ability to complex metal ions.
25

Zeolite and carbonate (carbonate (including bicarbonate and sesquicarbonate)) are preferred builders with carbonates being particularly preferred.
30

The composition may contain as builder a crystalline aluminosilicate, preferably an alkali metal aluminosilicate, more preferably a sodium aluminosilicate. This is typically present at a level of less than 15%w. Aluminosilicates are materials having the general formula:
35



where M is a monovalent cation, preferably sodium. These materials contain some bound water and are required to have a calcium ion exchange capacity of at least
5 50 mg CaO/g. The preferred sodium aluminosilicates contain 1.5-3.5 SiO₂ units in the formula above. They can be prepared readily by reaction between sodium silicate and sodium aluminate, as amply described in the literature. The ratio of surfactants to aluminosilicate (where present) is preferably greater than 5:2, more preferably greater than 3:1.

10

Alternatively, or additionally to the aluminosilicate builders, phosphate builders may be used. In this art the term 'phosphate' embraces diphosphate, triphosphate, and phosphonate species. Other forms of builder include silicates, such as soluble silicates, metasilicates, layered silicates (e.g. SKS-6 from Hoechst).

15

Preferably the laundry detergent formulation is a non-phosphate built laundry detergent formulation, i.e., contains less than 1 wt% of phosphate. Preferably powder laundry detergent formulations are predominantly carbonate built. Powders, should preferably give an in use pH of 9.5-11.

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Most preferably the laundry detergent is an aqueous liquid laundry detergent, preferably with a pH of from 7 to 9.

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

Fluorescent Agent

30 The composition preferably comprises a fluorescent agent (optical brightener). Fluorescent agents are well known and many such fluorescent agents are available commercially. Usually, these fluorescent agents are supplied and used in the form of their alkali metal salts, for example, the sodium salts.

Preferred classes of 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.

5

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.

10

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 %.

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

20 **Perfume**

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

25

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

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acetate; cedry formate; cyclohexyl salicylate; gamma-dodecalactone; and, beta phenylethyl phenyl acetate.

Useful components of the perfume include materials of both natural and synthetic origin.

- 5 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).
- 10 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.
- 15 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.
- 20 The International Fragrance Association has published a list of fragrance ingredients (perfums) in 2011. (<http://www.ifraorg.org/en-us/ingredients#.U7Z4hPldWzk>)
- The Research Institute for Fragrance Materials provides a database of perfumes (fragrances) with safety information.
- 25 Perfume top note may be used to cue the whiteness and brightness benefit of the invention.
- 30 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,
 5 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,
 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
 10 phenyl acetate, eucalyptol, eugenol, fenchyl acetate, flor acetate (tricyclo 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
 15 anthranilate, methyl benzoate, methyl benyl acetate, methyl eugenol, methyl heptenone,
 methyl heptine carbonate, methyl heptyl ketone, methyl hexyl ketone, methyl phenyl
 carbinyl 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
 20 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. 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
 25 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, including components of essential oils such as Clary Sage, Eucalyptus,
 30 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.

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.

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).

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

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-mercerised woven cotton sheeting.

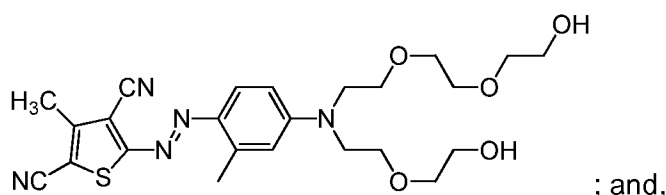
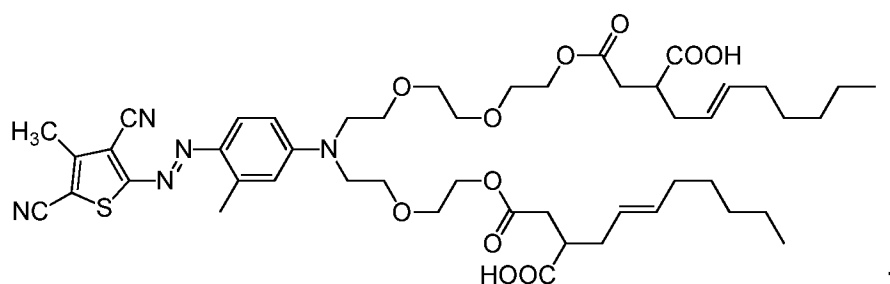
Shading dyes are discussed in WO2005/003274, WO2006/032327(Unilever), WO 2006/032397(Unilever), WO2006/045275(Unilever), WO 2006/027086(Unilever),

WO 2008/017570(Unilever), WO 2008/141880 (Unilever), WO2009/132870(Unilever), WO 2009/141173 (Unilever), WO 2010/099997(Unilever), WO 2010/102861(Unilever), WO 2010/148624(Unilever), WO2008/087497 (P&G), WO2011/011799 (P&G), WO2012/054820 (P&G), WO2013/142495 (P&G) and WO2013/151970 (P&G).

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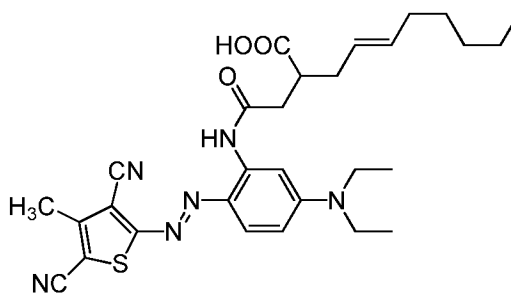
Mono-azo dyes preferably contain a heterocyclic ring and are most preferably thiophene dyes. The mono-azo dyes are preferably alkoxyated and are preferably uncharged or anionically charged at pH=7. Alkoxyated thiophene dyes are discussed in WO/2013/142495 and WO/2008/087497. Preferred examples of thiophene dyes are shown below:

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; and,

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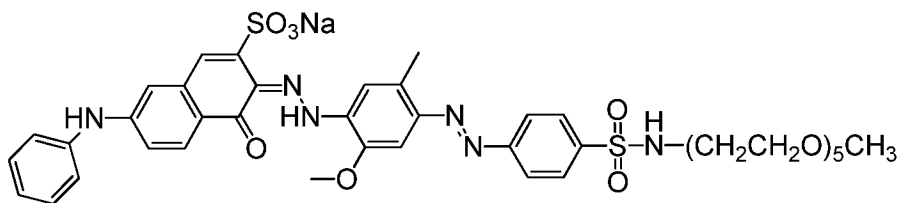


Bis-azo dyes are preferably sulphonated bis-azo dyes. Preferred examples of sulphonated bis-azo compounds are direct violet 7, direct violet 9, direct violet 11, direct violet 26, direct violet 31, direct violet 35, direct violet 40, direct violet 41, direct violet 51, Direct Violet 66, direct violet 99 and alkoxyated versions thereof. Alkoxyated bis-azo dyes are discussed in WO2012/054058 and WO2010/151906.

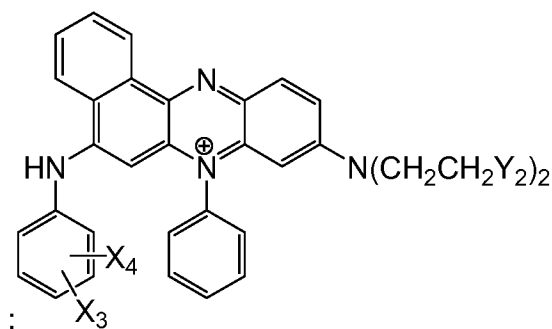
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- 15 -

An example of an alkoxyated bis-azo dye is :



- 5 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:



10

wherein:

X_3 is selected from: -H; -F; -CH₃; -C₂H₅; -OCH₃; and, -OC₂H₅;

- 15 X_4 is selected from: -H; -CH₃; -C₂H₅; -OCH₃; and, -OC₂H₅;

Y_2 is selected from: -OH; -OCH₂CH₂OH; -CH(OH)CH₂OH; -OC(O)CH₃; and, C(O)OCH₃.

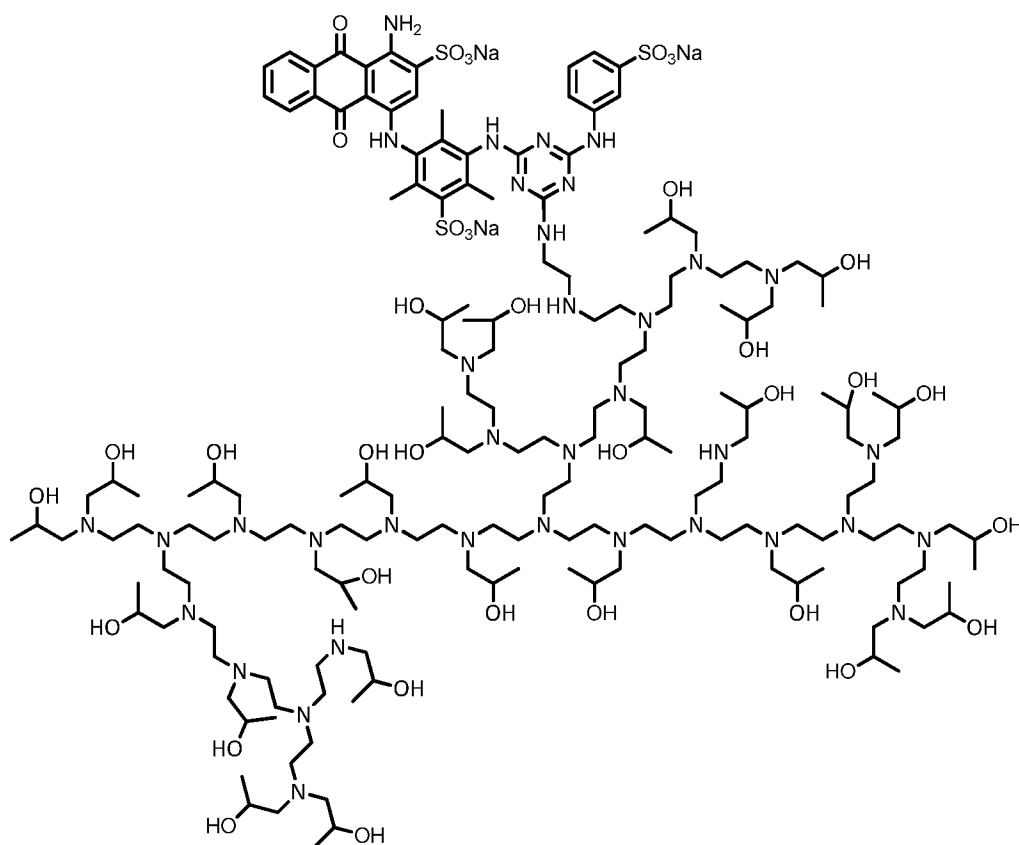
- 20 The shading dye is present in the composition in range from 0.0001 to 0.5 wt %, preferably 0.001 to 0.1 wt%. Depending upon the nature of the shading dye there are preferred ranges depending upon the efficacy of the shading dye which is dependent on class and particular efficacy within any particular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

- 25 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

5 by propoxylation. Preferably the polyethylene imine before reaction with the dye and the propoxylation has a molecular weight of 600 to 1800.

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



(Structure I).

- 15 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 blue101; Reactive blue103; Reactive blue114; Reactive blue117; Reactive blue125; Reactive blue141; Reactive blue142; Reactive blue 145; Reactive blue 149; Reactive blue 155; Reactive blue 164; Reactive blue 166; Reactive blue 177;
 5 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.

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

Protease Enzyme

Protease enzymes hydrolyse bonds within peptides and proteins, in the laundry context
 15 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 (<http://merops.sanger.ac.uk/>). Serine proteases are preferred. Subtilase type serine
 20 proteases are more preferred. The term "subtilases" refers to a sub-group of serine protease according to Siezen et al., Protein Engng. 4 (1991) 719-737 and Siezen et al. Protein Science 6 (1997) 501 -523. Serine proteases are a subgroup of proteases characterized by having a serine in the active site, which forms a covalent adduct with the
 25 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.

Examples of subtilases are those derived from Bacillus such as Bacillus lentus, B. alkalophilus, B. subtilis, B. amyloliquefaciens, Bacillus pumilus and Bacillus gibsonii
 30 described in; US7262042 and WO09/021867, and subtilisin lentus, subtilisin Novo, subtilisin Carlsberg, Bacillus licheniformis, subtilisin BPN', subtilisin 309, subtilisin 147 and subtilisin 168 described in WO89/06279 and protease PD138 described in (WO93/18140). Other useful proteases may be those described in W092/175177, WO01/016285, WO02/026024 and WO02/016547. Examples of trypsin-like proteases
 35 are trypsin (e.g. of porcine or bovine 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.

Further Examples of useful proteases are the variants described in: WO92/19729,
 5 WO96/034946, WO98/201 15, WO98/201 16, WO99/01 1768, WO01/44452,
 WO03/006602, WO04/03186, WO04/041979, WO07/006305, WO1 1/036263, WO1
 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, 118, 120, 123, 128, 129, 130, 160, 167, 170, 194, 195, 199, 205, 206, 217, 218,
 10 222, 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, G1 18V,R, H120D,N, N123S, S128L, P129Q, S130A, G160D, Y167A,
 R170S, A194P, G195E, V199M, V205I, L217D, N218D, M222S, A232V, K235L, Q236H,
 15 Q245R, N252K, T274A (using BPN' numbering).

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

Examples of subtilases are those derived from *Bacillus* such as *Bacillus lentus*, B.
 20 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*
 25 *lentus*, *B. alkalophilus*, *B. subtilis*, *B. amyloliquefaciens*, *Bacillus pumilus* and *Bacillus*
gibsonii as described in US 6,312,936 B1, 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.

30 Suitable commercially available protease enzymes include those sold under the trade
 names names Alcalase®, Blaze®; Duralase™, Durazym™, Relase®, Relase® Ultra,
 Savinase®, Savinase® Ultra, Primase®, Polarzyme®, Kannase®, Liqueanase®,
 Liqueanase® Ultra, Ovozyme®, Coronase®, Coronase® Ultra, Neutrase®, Everlase® and
 Esperase® all could be sold as Ultra® or Ecity® (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®, Preferenz™, Purafect MA®, Purafect Ox®, Purafect OXP®, Puramax®, Properase®, Effectenz™, 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 + V104I + G159S, hereinafter referred to as BLAP), BLAP R (BLAP with S3T + V4I + V199M + V205I + L217D), BLAP X (BLAP with S3T + V4I + V205I) and BLAP F49 (BLAP with S3T + V4I + A194P + V199M + V205I + L217D) - all from Henkel/Kemira; and KAP (Bacillus
- 15 alkalophilus subtilisin with mutations A230V + S256G + S259N) from Kao.

Further Enzymes

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

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

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

- 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 A₁ 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
35 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.).

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, 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.

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).

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

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.

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.

5 **Experimental**

Example 1

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

Ingredient	Weight%
Mono propylene glycol	2.2
Triethylamine	1.5
C12-C15 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 ₂ dihydrate	0.2
NaCl	0.2
Tinopal CBS-X (fluorescer BASF)	0.3
Sodium Hydroxide	To pH=8.4
ASP dispersant	See text
Water	balance

10

The formulation was used to wash eight 5x5cm EMPA 117 stain monitor (blood/milk/ink stain on polycotton) in a tergotometer set at 200rpm. A 20 minute wash was conducted in 800ml of 26o French Hard water at 25oC, with 2.3g/L of the formulation. To simulate oily soil (7.2g) of an SBL2004 soil strip (ex Warwick Equest) was added to the wash liquor.

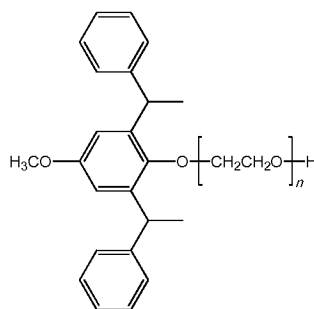
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Once the wash had been completed the cotton monitors were rinsed once in 400ml clean water, removed dried and the colour measured on a reflectometer and expressed as the CIE L*a*b* values.

20

Equivalent Formulations but with the addition of 8.7 wt% of the ASP dispersant (n = 20):

- 23 -



Experiments were repeated with and without the addition of a subtilisin serine protease ((EC no. 232-752-2) to the wash liquor (Evity® 16L ex Novozymes). The enzyme was added to give 0.009 wt % pure active protein to the formulation.

95% confidence limits are also given calculated from the standard deviation on the measurements from the 8 monitors.

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

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

The larger the ΔL value the greater the prevention of deposition of the carbon black soil. 95% confidence limits based on the 8 separate cotton monitors were calculated. Formulations were made with and without the addition of 8.7wt% of the dispersant:

The cleaning benefit was expressed as the ΔL value:

$$\Delta L = L(\text{test}) - L(\text{control})$$

The larger the ΔL value the greater the prevention of deposition of the carbon black soil

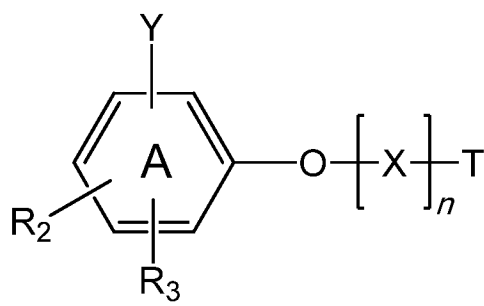
test	ΔL	95%
Protease	1.55	0.60
ASP dispersant	1.32	0.41
Protease + ASP dispersant	4.05	0.44

The ASP dispersant alone and the protease alone enhance stains removal. A further increase is seen when the 2 are combined and $\Delta L = 4.05$ is larger than expected by summing the individual performance, $1.55 + 1.32 = 2.88$.

CLAIMS

1. A laundry detergent composition comprising:

- 5 (i) from 0.5 to 20 wt% of an alkoxyated substituted phenol dispersant of the following structure:



wherein

10

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;

15

Y is selected from: R₁; OR₁; COOR₅; F; Cl; Br; I; CN; and NO₂, wherein R₁ is a C1 to C4 linear or branched alkyl group and R₅ is selected from C1 to C18 linear or branched alkyl groups;

20

R₂ and R₃ are selected from: C1 to C3 linear or branched alkyl aryl groups; and, aryl groups;

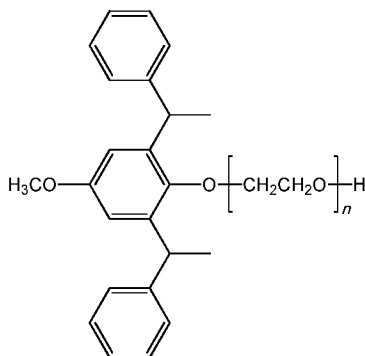
T is selected from: H; CH₃; SO₃⁻; CH₂COO⁻; PO₃²⁻; C₂H₅; n-propyl, i-propyl; n-butyl; t-butyl; and, sulfosuccinate;

25

- (ii) from 0 to 50 wt% surfactant, other than the alkoxyated substituted phenol; and,
- (iii) from 0.0005 to 0.2 wt% of a protease enzyme.

2. A laundry detergent composition according to claim 1, wherein R₂ and R₃ are selected from styryl and cumyl,
3. A laundry detergent composition according to claim 1, wherein R₂ and R₃ are styryl
5 and both R₂ and R₃ are in the ortho position to the -O-[X]_n-T group.
4. A laundry detergent composition according to claim 1, 2 or 3, wherein X is ethoxy.
5. A laundry detergent composition according to any one of the preceding claims,
10 wherein n is from 8 to 34.
6. A laundry detergent composition according to any one of the preceding claims, wherein the surfactant is selected from: anionic and non-ionic surfactants and the level of surfactant is from 4 to 40 wt%.
15
7. A laundry detergent composition according to any one of the preceding claims, wherein the weight fraction of non-ionic surfactant/anionic surfactant is from 0 to 0.3.
- 20 8. A laundry detergent composition according claim 6 or 7, wherein the anionic surfactant is selected from: linear alkyl benzene sulphonates; alkyl sulphates; and, alkyl ether sulphates; and mixtures thereof.
9. A laundry detergent composition according to any one of the preceding claims,
25 wherein the level of the alkoxyated substituted phenol dispersant from 1 to 10 wt%.
10. A laundry detergent composition according to any one of the preceding claims, wherein T is H.
- 30 11. A laundry detergent composition according to any one of the preceding claims, wherein the Y is selected from: methyl; ethyl; methoxy; and, ethoxy.
12. A laundry detergent composition according to claim 1, wherein the the alkoxyated substituted phenol dispersant is:

- 27 -



and the protease enzyme is a subtilisin (EC 3.4.21.62).

5

13. A laundry detergent composition according to any one of the preceding claims, wherein n is selected from: 14; 15; 16; 17; 18; 19; 20; 21; 22; 23; 24; 25; 26; 27; 28; 29; 30; 31; and, 32.

10

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

(i) treating a textile with an aqueous solution of the alkoxy-substituted phenol dispersant the aqueous solution comprising from 10 ppm to 5000 ppm of the alkoxy-substituted phenol dispersant as defined in any one of the preceding claims; from 0.01 to 1ppm of a protease enzyme; and, 0 to 6 g/L of a surfactant, other than the alkoxy-substituted phenol dispersant; and,

15

(ii) optionally rinsing and drying the textile.

20

15. A domestic method of treating a textile according to claim 14 wherein in the method the protease enzyme is a subtilisin (EC 3.4.21.62).

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2016/078515

A. CLASSIFICATION OF SUBJECT MATTER INV. C11D1/37 C11D1/83 C11D3/386 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) 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.
A	WO 2012/054820 A1 (PROCTER & GAMBLE [US]; STENGER PATRICK CHRISTOPHER [US]; MIRACLE GREGO) 26 April 2012 (2012-04-26) cited in the application page 1, lines 6-10 page 2, line 5 - page 3, line 12 page 5, line 12 - page 17, line 10 page 21, line 31 - page 23, line 33 page 27, lines 3-10; examples 1,6 -----	1-15
A	GB 2 007 692 A (RHONE POULENC IND) 23 May 1979 (1979-05-23) page 1, lines 3-5 page 2, line 55 - page 3, line 8 -----	1-15
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "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 "&" document member of the same patent family		
Date of the actual completion of the international search 31 January 2017		Date of mailing of the international search report 08/02/2017
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 Marttin, Emmeline

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2016/078515

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