(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 3 417 042 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
07.08.2019 Bulletin 2019/32

(21) Application number: **16805031.8**

(22) Date of filing: **22.11.2016**

(51) Int Cl.:
C11D 3/20 *(2006.01)* ***C11D 3/42*** *(2006.01)*
C11D 3/50 *(2006.01)* ***C11D 1/37*** *(2006.01)*
C11D 1/83 *(2006.01)* ***C11D 3/40*** *(2006.01)*

(86) International application number:
PCT/EP2016/078457

(87) International publication number:
WO 2017/140390 (24.08.2017 Gazette 2017/34)

(54) **WHITENING COMPOSITION**

BLEICHUNGSZUSAMMENSETZUNG

COMPOSITION DE BLANCHIMENT

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

(30) Priority: **17.02.2016 EP 16156029**

(43) Date of publication of application:
26.12.2018 Bulletin 2018/52

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  AL AT BE BG CH CZ DE DK EE ES FI FR GR HR HU IS IT LI LT LU LV MC MK NL NO PL PT RO RS SE SI SK SM TR

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EP 3 417 042 B1

Description

Field of Invention

[0001] The present invention concerns the use of whitening and brightening laundry compositions.

Background of the Invention

[0002] Maintaining and improving the whiteness and brightness of textiles during domestic laundry is desirable. A problem is the redeposition of soil removed from one garment onto another. 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. This process leads to an overall loss of whiteness and cleaning across the washing load. There is a need for weight effective agents laundry benefit agents that reduce the redeposition of soil whilst also increasing stain removal. Such ingredients are preferably biodegradable.

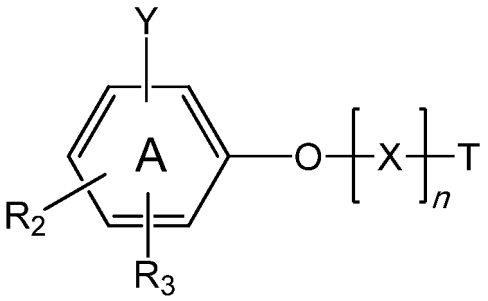
Summary of the Invention

[0003] There is a need for technologies to reduce redeposition and enhance cleaning in domestic laundry products.

[0004] We have found that selected alkoxylated substituted phenol (ASP) dispersants when incorporated into laundry detergents enhance whiteness and brightness of garments during domestic laundering.

[0005] In one aspect the present invention provides a laundry detergent composition comprising:

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



,

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 R5 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 alkoxylated 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 0.001 to 3 wt % perfume.

[0006] Interger (iii), the perfume, may be replaced or 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.

[0007] 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.

[0008] In another aspect the present 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 alkoxylated substituted phenol dispersant the aqueous solution comprising from 10 ppm to 5000 ppm of the alkoxylated substituted phenol dispersant, preferably from 100 ppm to 1000 ppm as defined herein; and, 0 to 6 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.

[0009] In the method the surfactant is of the type as preferred herein.

[0010] 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.

[0011] In the method aspects of the present invention the surfactant used is preferably as preferred for the composition aspects of the present invention.

[0012] Domestic methods are preferably conducted in a domestic washing machine or by hand washing. The temperature of the wash is preferably from 285 to 335K.
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

Alkoxylated Substituted Phenol

[0013] 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.

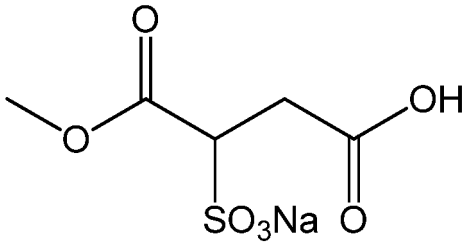
[0014] The most preferred aryl groups are phenyl and substituted phenyl.

[0015] 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.

[0016] A styryl group is -$CH(CH_3)Ph$; a cumyl group is -$C(CH_3)_2Ph$; a benzyl group is CH_2Ph, where Ph is phenyl.

[0017] The value n is the mole average number of alkoxyl groups. The value of n may be measured using NMR.

[0018] Sulfoccinate has the structure, depicted as the Na salt:



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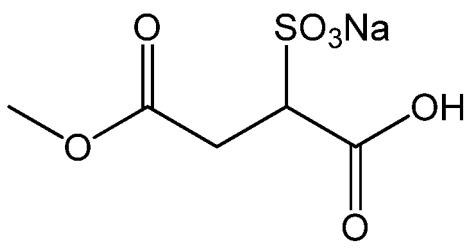

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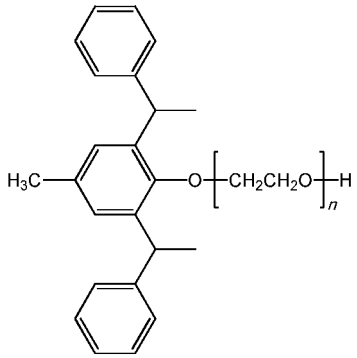
[0019] Example of structures of the ASP of the invention are:



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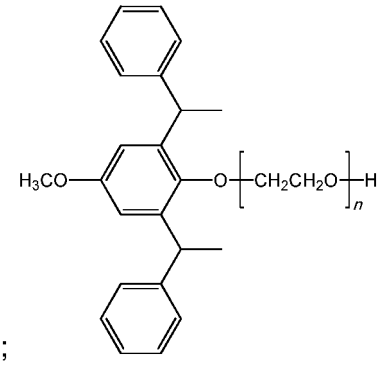

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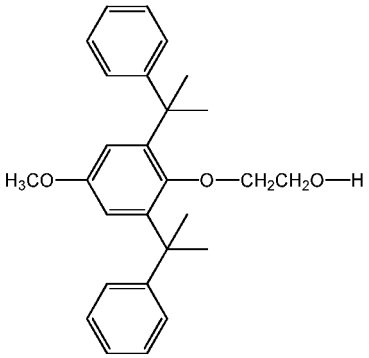

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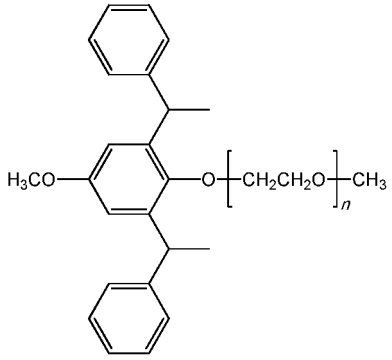

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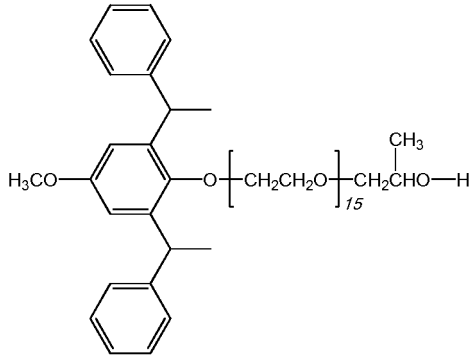

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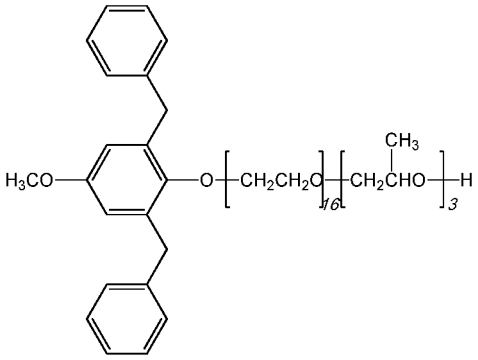
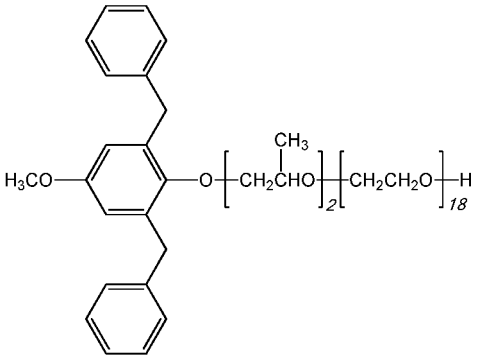
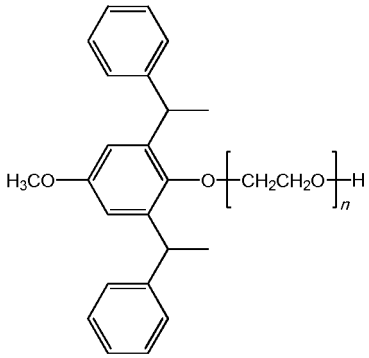




; and, .

[0020] The most preferred ASP structure is



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Surfactant

[0021] The laundry composition may comprises anionic and non-ionic surfactant (which includes a mixture of the same).

[0022] 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 "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) .

[0023] 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.

[0024] Examples of suitable synthetic anionic detergent compounds are sodium and potassium alkyl sulphates, especially those obtained by sulphating higher C_8 to C_{18} alcohols, produced for example from tallow or coconut oil, sodium and potassium alkyl C_9 to C_{20} benzene sulphonates, particularly sodium linear secondary alkyl C_{10} to C_{15} 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.

[0025] 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.

[0026] The most 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_{12}-C_{14} 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_{11} to C_{15} alkyl benzene sulphonates. Preferably the alkyl sulphates is a linear or branched sodium C_{12} to C_{18} alkyl sulphates. Sodium dodecyl sulphate is particularly preferred, (SDS, also known as primary alkyl sulphate).

[0027] 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%.

[0028] Preferably two or more anionic surfactant are present, for example linear alkyl benzene sulphonate together with an alkyl ether sulphate.

[0029] Preferably the laundry composition in addition to the anionic surfactant comprises alkyl ethoxylated non-ionic surfactant-.

[0030] 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 the condensation products of aliphatic C_8 to C_{18} primary or secondary linear or branched alcohols with ethylene oxide.

[0031] Preferably the alkyl ethoxylated non-ionic surfactant is a C_8 to C_{18} primary alcohol with an average ethoxylation of 7EO to 9EO units.

[0032] Preferably the surfactants used are saturated.

[0033] 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.

[0034] In another aspect the charged surfactant may be a cationic such that the formulation is a fabric conditioner. The detergent compositions based on anionic or anionic/non-ionic surfactants is however the more preferred embodiment.

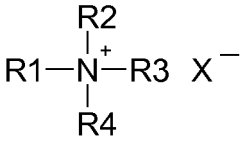
Cationic Compound

[0035] When the present invention is used as a fabric conditioner it needs to contain a cationic compound.

[0036] Most preferred are quaternary ammonium compounds.

[0037] It is advantageous if the quaternary ammonium compound is a quaternary ammonium compound having at least one C_{12} to C_{22} alkyl chain.

[0038] It is preferred if the quaternary ammonium compound has the following formula:



in which R_1 is a C_{12} to C_{22} alkyl or alkenyl chain; R^2, R^3 and R^4 are independently selected from C_1 to C_4 alkyl chains and X^- is a compatible anion. A preferred compound of this type is the quaternary ammonium compound cetyl trimethyl quaternary ammonium bromide.

[0039] A second class of materials for use with the present invention are the quaternary ammonium of the above structure in which R^1 and R^2 are independently selected from C_{12} to C_{22} alkyl or alkenyl chain; R^3 and R^4 are independently selected from C_1 to C_4 alkyl chains and X^- is a compatible anion.

[0040] The composition optionally comprises a silicone.

Builders or Complexing Agents

[0041] Builder materials may be selected from 1) calcium sequestrant materials, 2) precipitating materials, 3) calcium ion-exchange materials and 4) mixtures thereof.

[0042] Examples of calcium sequestrant builder materials include alkali metal polyphosphates, such as sodium tripolyphosphate and organic sequestrants, such as ethylene diamine tetra-acetic acid.

[0043] Examples of precipitating builder materials include sodium orthophosphate and sodium carbonate.

[0044] 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.

[0045] 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.

[0046] Zeolite and carbonate (carbonate (including bicarbonate and sesquicarbonate)) are preferred builders with carbonates being particularly preferred.

[0047] 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:

$$0.8\text{-}1.5M_2O.\ Al_2O_3.\ 0.8\text{-}6\ SiO_2$$

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 50 mg CaO/g. The preferred sodium aluminosilicates contain 1.5-3.5 SiO_2 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 alumuminosilicate (where present) is preferably greater than 5:2, more preferably greater than 3:1.

[0048] 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).

[0049] 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 to 11.

[0050] Most preferably the laundry detergent is an aqueous liquid laundry detergent, preferably with a pH of from 7 to 9.

[0051] 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%, to provide the formulation with appropriate, pourable viscosity.

Fluorescent Agent

[0052] 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.

[0053] Preferred classes of fluorescer are: Di-styryl biphenyl compounds, e.g. Tinopal (Trade Mark) CBS-X, Di-amine stilbene di-sulphonic acid compounds, e.g. Tinopal DMS pure Xtra and Blankophor (Trade Mark) HRH, and Pyrazoline compounds, e.g. Blankophor SN.

[0054] Preferred fluorescers are: sodium 2 (4-styryl-3-sulphophenyl)-2H-napthol[1,2-d]triazole, disodium 4,4'-bis{[(4-anilino-6-(N methyl-N-2 hydroxyethyl) amino 1,3,5-triazin-2-yl)]amino}stilbene-2-2' disulophonate, 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.

[0055] 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 %.

[0056] The aqueous solution used in the method has a fluorescer present. The fluorescer is present in the aqueous solution used in the method preferably in the range from 0.0001 g/l to 0.1 g/l, more preferably 0.001 to 0.02 g/l.

Perfume

[0057] The composition comprises a perfume. The perfume is preferably in the range from 0.001 to 3 wt %, more

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

[0058] 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 acetate; cedry formate; cyclohexyl salicyate; gamma-dodecalactone; and, beta phenylethyl phenyl acetate.

[0059] Useful components of the perfume include materials of both natural and synthetic origin. They include single compounds and mixtures. Specific examples of such components may be found in the current literature, e.g., in Fenaroli's Handbook of Flavor Ingredients, 1975, CRC Press; Synthetic Food Adjuncts, 1947 by M. B. Jacobs, edited by Van Nostrand; or Perfume and Flavor Chemicals by S. Arctander 1969, Montclair, N.J. (USA).

[0060] 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.

[0061] 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.

[0062] The International Fragrance Association has published a list of fragrance ingredients (perfums) in 2011. (http://www.ifraorg.org/en-us/ingredients#.U7Z4hPldWzk)

[0063] The Research Institute for Fragrance Materials provides a database of perfumes (fragrances) with safety information.

[0064] Perfume top note may be used to cue the whiteness and brightness benefit of the invention.

[0065] Some or all of the perfume may be encapsulated, typical perfume components which it is advantageous to encapsulate, include those with a relatively low boiling point, preferably those with a boiling point of less than 300, preferably 100-250 Celsius. It is also advantageous to encapsulate perfume components which have a low CLog P (ie. those which will have a greater tendency to be partitioned into water), preferably with a CLog P of less than 3.0. These materials, of relatively low boiling point and relatively low CLog P have been called the "delayed blooming" perfume ingredients and include one or more of the following materials:

allyl caproate, amyl acetate, amyl propionate, anisic aldehyde, anisole, benzaldehyde, benzyl acetate, benzyl acetone, benzyl alcohol, benzyl formate, benzyl iso valerate, benzyl propionate, beta gamma hexenol, camphor gum, laevo-carvone, d-carvone, cinnamic alcohol, cinamyl formate, cis-jasmone, cis-3-hexenyl acetate, cuminic alcohol, cyclal c, dimethyl benzyl carbinol, dimethyl benzyl carbinol acetate, ethyl acetate, ethyl aceto acetate, ethyl amyl ketone, ethyl benzoate, ethyl butyrate, ethyl hexyl ketone, ethyl phenyl acetate, eucalyptol, eugenol, fenchyl acetate, flor acetate (tricyclo decenyl acetate), frutene (tricyclco decenyl propionate), geraniol, hexenol, hexenyl acetate, hexyl acetate, hexyl formate, hydratropic alcohol, hydroxycitronellal, indone, isoamyl alcohol, iso menthone, isopulegyl acetate, isoquinolone, ligustral, linalool, linalool oxide, linalyl formate, menthone, menthyl acetphenone, methyl amyl ketone, methyl anthranilate, methyl benzoate, methyl benyl acetate, methyl eugenol, methyl heptenone, methyl heptine 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 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 the list given of delayed blooming perfumes given above present in the perfume.

[0066] Another group of perfumes with which the present invention can be applied are the so-called 'aromatherapy' materials. These include many components also used in perfumery, including components of essential oils such as Clary Sage, Eucalyptus, Geranium, Lavender, Mace Extract, Neroli, Nutmeg, Spearmint, Sweet Violet Leaf and Valerian. It is preferred that the laundry treatment composition does not contain a peroxygen bleach, e.g., sodium percarbonate, sodium perborate, and peracid.

Polymers

[0067] 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.

[0068] Polymers present to prevent dye deposition may be present, for example poly(vinylpyrrolidone), poly(vinylpyridine-N-oxide), and poly(vinylimidazole).

Shading Dye

[0069] Dyes are described in Color Chemistry Synthesis, Properties and Applications of Organic Dyes and Pigments, (H Zollinger, Wiley VCH, Zurich, 2003) and, Industrial Dyes Chemistry, Properties Applications. (K Hunger (ed), Wiley-VCH Weinheim 2003).

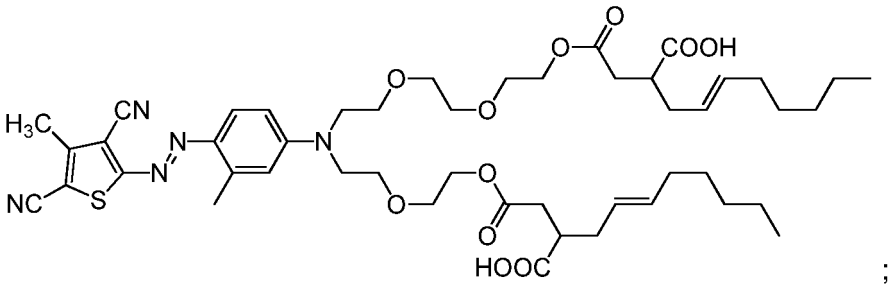
[0070] Shading Dyes for use in laundry detergents preferably have an extinction coefficient at the maximum absorption in the visible range (400 to 700nm) of greater than 5000 L mol^{-1} cm^{-1}, preferably greater than 10000 L mol^{-1} cm^{-1}. The dyes are blue or violet in colour.

[0071] Preferred shading dye chromophores are azo, azine, anthraquinone, and triphenylmethane.

[0072] 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.

[0073] 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).

[0074] Mono-azo dyes preferably contain a heterocyclic ring and are most preferably thiophene dyes. The mono-azo dyes are preferably alkoxylated and are preferably uncharged or anionically charged at pH=7. Alkoxylated thiophene dyes are discussed in WO/2013/142495 and WO/2008/087497. Preferred examples of thiophene dyes are shown below:



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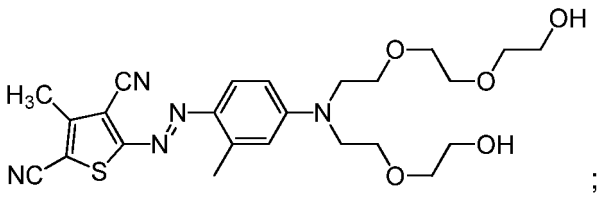
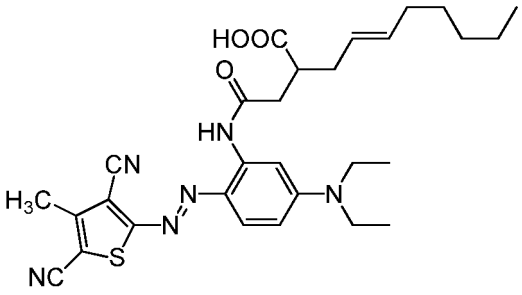


;

and,



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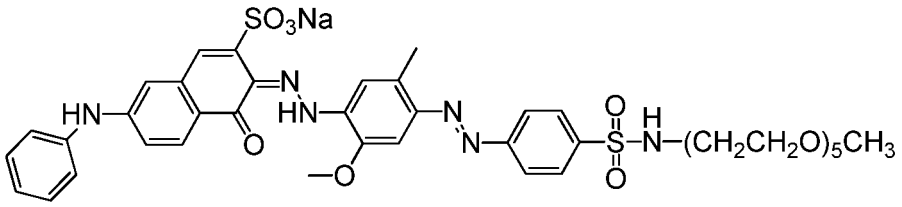
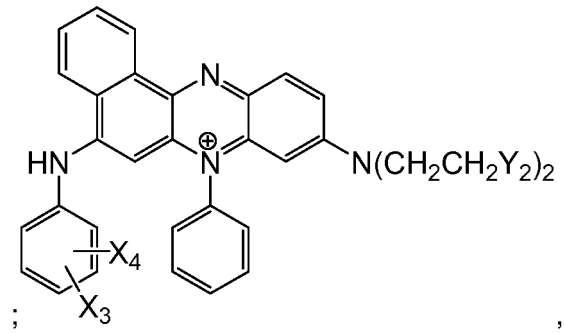
[0075] Bis-azo dyes are preferably sulphonated bis-azo dyes. Preferred examples of sulphonated bis-azo compounds are direct violet 7, direct violet 9, direct violet 11, direct violet 26, direct violet 31, direct violet 35, direct violet 40, direct violet 41, direct violet 51, Direct Violet 66, direct violet 99 and alkoxylated versions thereof. Alkoxylated bis-azo dyes are discussed in WO2012/054058 and WO2010/151906.

[0076] An example of an alkoxylated bis-azo dye is :



.

[0077] 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; $-CH_3$; $-C_2H_5$; $-OCH_3$; and, $-OC_2H_5$;

X_4 is selected from: -H; $-CH_3$; $-C_2H_5$; $-OCH_3$; and, $-OC_2H_5$;

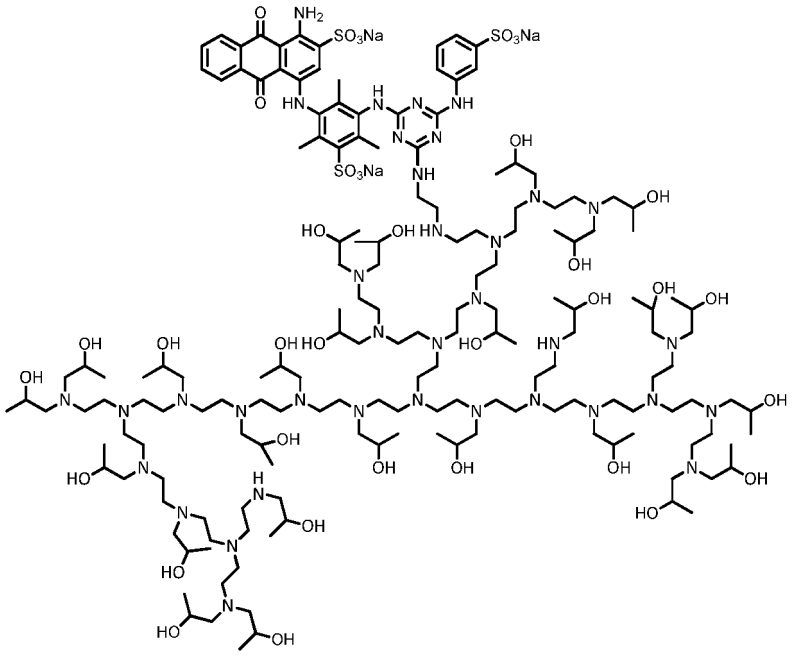
Y_2 is selected from: -OH; $-OCH_2CH_2OH$; $-CH(OH)CH_2OH$; $-OC(O)CH_3$; and, $C(O)OCH_3$.

[0078] The shading dye is present is present in the composition in range from 0.0001 to 0.5 wt %, preferably 0.001 to 0.1 wt%. Depending upon the nature of the shading dye there are preferred ranges depending upon the efficacy of the shading dye which is dependent on class and particular efficacy within any particular class. As stated above the shading dye is a blue or violet shading dye.

[0079] A mixture of shading dyes may be used.

[0080] The shading dye is most preferably a reactive blue anthraquinone dye covalently linked to an alkoxylated 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.

[0081] An example structure of a preferred reactive anthraquinone covalently attached to a propoxylated polyethylene imine is:



(Structure I).

[0082] 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; 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.

[0083] The dyes are listed according to Colour Index (Society of Dyers and Colourists/American Association of Textile Chemists and Colorists) classification.

Enzymes

[0084] One or more enzymes are preferred present in a laundry composition of the invention and when practicing a method of the invention.

[0085] Preferably the level of each enzyme in the laundry composition of the invention is from 0.0001 wt% to 0.1 wt% protein.

[0086] Preferably the enzyme is selected from: proteases; lipases; and, cellulases, preferably a protease.

[0087] Especially contemplated enzymes include proteases, alpha-amylases, cellulases, lipases, peroxidases/oxidases, pectate lyases, and mannanases, or mixtures thereof.

[0088] Suitable lipases include those of bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Examples of useful lipases include lipases from *Humicola* (synonym *Thermomyces*), e.g. from *H. lanuginosa* (*T. lanuginosus*) as described in EP 258 068 and EP 305 216 or from *H. insolens* as described in WO 96/13580, a *Pseudomonas* lipase, e.g. from *P. alcaligenes* or *P. pseudoalcaligenes* (EP 218 272), *P. cepacia* (EP 331 376), *P. stutzeri* (GB 1,372,034), *P. fluorescens, Pseudomonas* sp. strain SD 705 (WO 95/06720 and WO 96/27002), *P. wisconsinensis* (WO 96/12012), a *Bacillus* lipase, e.g. from *B. subtilis* (Dartois et al. (1993), Biochemica et Biophysica Acta, 1131, 253-360), *B. stearothermophilus* (JP 64/744992) or B. *pumilus* (WO 91/16422).

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

[0089] Preferred commercially available lipase enzymes include Lipolase™ and Lipolase Ultra™, Lipex™ and Lipoclean™ (Novozymes A/S).

[0090] 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.

[0091] 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 phospholipases A_1 and A_2 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.

[0092] Suitable proteases include those of animal, vegetable or microbial origin. Microbial origin is preferred. Chemically modified or protein engineered mutants are included. The protease may be a serine protease or a metallo protease, preferably an alkaline microbial protease or a trypsin-like protease. Preferred commercially available protease enzymes include Alcalase™, Savinase™, Primase™, Duralase™, Dyrazym™, Esperase™, Everlase™, Polarzyme™, and Kannase™, (Novozymes A/S), Maxatase™, Maxacal™, Maxapem™, Properase™, Purafect™, Purafect OxP™, FN2™, and FN3™ (Genencor International Inc.).

[0093] 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.

[0094] Suitable amylases (alpha and/or beta) include those of bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Amylases include, for example, alpha-amylases obtained from *Bacillus,* e.g. a special strain of *B. licheniformis,* described in more detail in GB 1,296,839, or the *Bacillus* sp. strains disclosed in WO 95/026397 or WO 00/060060. Commercially available amylases are Duramyl™, Termamyl™, Termamyl Ultra™, Natalase™, Stainzyme™, Fungamyl™ and BAN™ (Novozymes A/S), Rapidase™ and Purastar™ (from Genencor International Inc.).

[0095] 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.

[0096] 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).

[0097] Further enzymes suitable for use are discussed in WO2009/087524, WO2009/090576, WO2009/107091, WO2009/111258 and WO2009/148983.

Enzyme Stabilizers

[0098] 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.

[0099] 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.

[0100] 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

Example 1 redeposition benefit

[0101] An aqueous liquid laundry detergent was prepared of the following formulation:

Ingredient	Weight%
Mono propylene glycol	2.2
Triethylamine	1.5

(continued)

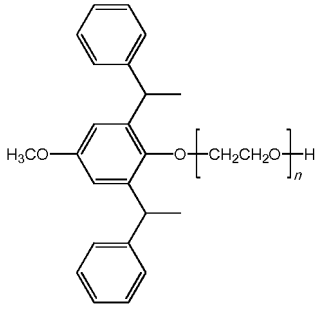
Ingredient	Weight%
C12-C15 alcohol ethoxylate with 7 moles of ethylene oxide	1.2
Linear alkyl benzene sulfonate	4.6
Sodium laureth ether sulphate with 1 moles of ethylene oxide	5.8
Citric acid	2.0
$CaCl_2$ dihydrate	0.2
NaCl	0.2
Tinopal CBS-X (fluorescer BASF)	0.3
Sodium Hydroxide	To pH=8.4
ASP dispersant	See text
Water	balance

[0102] The formulation was used to wash eight 5x5cm knitted cotton cloth pieces in a tergotometer set at 200rpm. A one hour wash was conducted in 800ml of 26° French Hard water at 20°C, with 2.3g/L of the formulation. To simulate soil that could redeposit, 0.04g/L of 100% compressed carbon black (ex Alfa Aesur) 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.

[0103] 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:

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

[0104] 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:



[0105] 3 different levels of ethoxylation were tested. The results are given in the table below.

n	ΔL	95%
10	4.40	0.44
20	2.29	0.45
30	4.04	0.43

[0106] The dispersant prevents deposition of the carbon black soil to the cotton cloth.

Example 2 stain removal benefit

[0107] The formulations of Example 1 was used to wash eight 5x5cm EMPA 117 stain monitor (blood/milk/ink stain on polycotton) in a tergotometer set at 200rpm. A 60 minute wash was conducted in 800ml of 26° French Hard water at 20°C, with 2.3g/L of the formulation. To simulate oily sebaceous soil (7.2 g) of an SBL2004 soil strip (ex Warwick Equest) was added to the wash liquor.

[0108] 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.

[0109] The cleaning benefit was expressed as the ΔL value:

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

[0110] The larger the ΔL value the greater the cleaning.

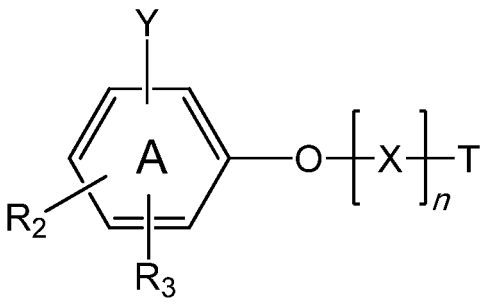
n	ΔL	95%
10	0.49	0.43
20	1.45	0.26
30	0.96	0.32

[0111] The dispersants enhance stain removal.

Claims

1. A laundry detergent composition comprising:

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



,

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;
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 R_5 is selected from C1 to C18 linear or branched alkyl groups;
R_2 and R_3 are selected from: C1 to C3 linear or branched alkyl aryl groups; and, aryl groups;
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;

(ii) from 0 to 50 wt% surfactant, other than the alkoxylated substituted phenol; 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 a fluorescent agent and/or from 0.0001 wt% to 0.1 wt% shading dye.

2. A laundry detergent composition according to claim 1, wherein R_2 and R_3 are selected from styryl and cumyl.

3. A laundry detergent composition according to claim 1, wherein R_2 and R_3 are styryl and both R_2 and R_3 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, 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%.

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.

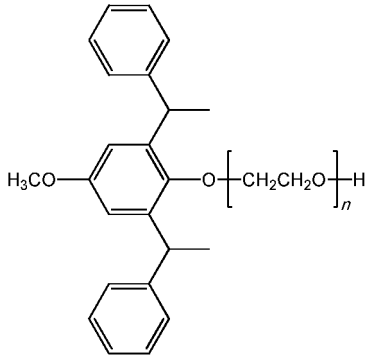
8. A laundry detergent composition according claim 6 or 7, wherein the anionic surfactant is selected from: linear alkyl benzene sulphonates; alkyl sulphates; and, alkyl ether sulphates; and mixtures thereof.

9. A laundry detergent composition according to any one of the preceding claims, wherein the level of the alkoxylated 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.

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 alkoxylated substituted phenol dispersant is:



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.

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

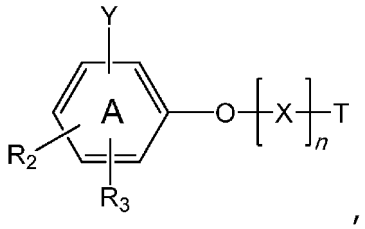
(i) treating a textile with an aqueous solution of the alkoxylated substituted phenol dispersant the aqueous solution comprising from 10 ppm to 5000 ppm of the alkoxylated substituted phenol dispersant as defined in any one of the preceding claims; and, 0 to 6 g/L of a surfactant, other than the alkoxylated substituted phenol dispersant; and,
(ii) optionally rinsing and drying the textile.

15. A domestic method of treating a textile according to claim 14 wherein the method the level of the perfume in the aqueous solution is preferably from 0.1 to 100 ppm.

Patentansprüche

1. Wäschewaschmittelzusammensetzung, umfassend:

(i) von 0,5 bis 20 Gew.-% eines alkoxylierten substituierten Phenol-Dispergiermittels der folgenden Struktur



worin

X ausgewählt ist aus: Ethoxy- und Mischungen von Ethoxy- und Propoxy-Gruppen, wobei die Anzahl der Ethoxy-Gruppen größer als die Anzahl der Propoxy-Gruppen ist, und worin n von 6 bis 70 beträgt;
Y ausgewählt ist aus: R_1; OR_1, $COOR_5$; F; Cl; Br; I; CN; und NO_2, worin R1 eine lineare oder verzweigte C_1- bis C_4-Alkylgruppe ist und R_5 aus linearen oder verzweigten C_1- bis C_{18}-Alkyl-Gruppen ausgewählt ist;
R_2 und R_3 ausgewählt sind aus: linearen oder verzweigten C_1- bis C_3-Alkylaryl-Gruppen und Aryl-Gruppen;
T ausgewählt ist aus: H; CH_3; SO_3^-; CH_2COO^-; PO_3^{2-}; C_2H_5; n-Propyl, i-Propyl; n-Butyl; t-Butyl; und Sulfosuccinat;

(ii) von 0 bis 50 Gew.-% Tensid, ausgenommen das alkoxylierte substituierte Phenol; und
(iii) ein aktives Mittel, ausgewählt aus einem oder mehreren von Folgenden: von 0,001 bis 3 Gew.-% Parfüm; von 0,0001 bis 0,5 Gew.-% eines Fluoreszenzmittels und/oder von 0,0001 Gew.-% bis 0,1 Gew.-% Nuancierfarbstoff.

2. Wäschewaschmittelzusammensetzung nach Anspruch 1, wobei R_2 und R_3 aus Styryl und Cumyl ausgewählt sind.

3. Wäschewaschmittelzusammensetzung nach Anspruch 1, wobei R_2 und R_3 Styryl sind und sich sowohl R_2 als auch R_3 in der Ortho-Stellung zu der -O-$[X]_n$-T-Gruppe befinden.

4. Wäschewaschmittelzusammensetzung nach Anspruch 1, 2 oder 3, wobei X Ethoxy ist.

5. Wäschewaschmittelzusammensetzung nach irgendeinem der vorhergehenden Ansprüche, wobei n von 8 bis 34 beträgt.

6. Wäschewaschmittelzusammensetzung nach irgendeinem der vorhergehenden Ansprüche, wobei das Tensid ausgewählt ist aus: anionischen und nicht-ionischen Tensiden und die Konzentration des Tensids von 4 bis 40 Gew.-% beträgt.

7. Wäschewaschmittelzusammensetzung nach irgendeinem der vorhergehenden Ansprüche, wobei die Gewichtsfraktion von nicht-ionischem Tensid/anionischem Tensid von 0 bis 0,3 beträgt.

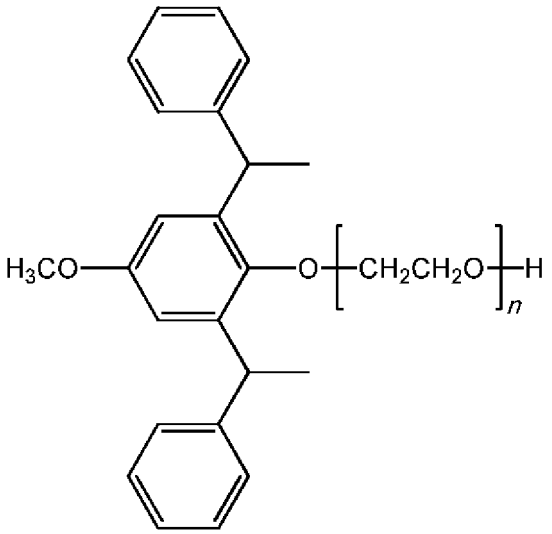
8. Wäschewaschmittelzusammensetzung nach Anspruch 6 oder 7, wobei das anionische Tensid ausgewählt ist aus: linearen Alkylbenzolsulfonaten; Alkylsulfaten; und Alkylethersulfaten und Mischungen davon.

9. Wäschewaschmittelzusammensetzung nach irgendeinem der vorhergehenden Ansprüche, wobei die Konzentration des alkoxylierten substituierten Phenol-Dispergiermittels von 1 bis 10 Gew.-% beträgt.

10. Wäschewaschmittelzusammensetzung nach irgendeinem der vorhergehenden Ansprüche, wobei T H ist.

11. Wäschewaschmittelzusammensetzung nach irgendeinem der vorhergehenden Ansprüche, wobei Y ausgewählt ist aus Methyl; Ethyl; Methoxy; und Ethoxy.

12. Wäschewaschmittelzusammensetzung nach Anspruch 1, wobei das alkoxylierte substituierte Phenol-Dispergiermittel ist:



13. Wäschewaschmittelzusammensetzung nach irgendeinem der vorhergehenden Ansprüche, wobei n ausgewählt ist aus: 14; 15; 16; 17; 18; 19; 20; 21; 22; 23; 24; 25; 26; 27; 28; 29; 30; 31 und 32.

14. Häusliches Verfahren zum Behandeln eines Textils, wobei das Verfahren die Schritte umfasst:

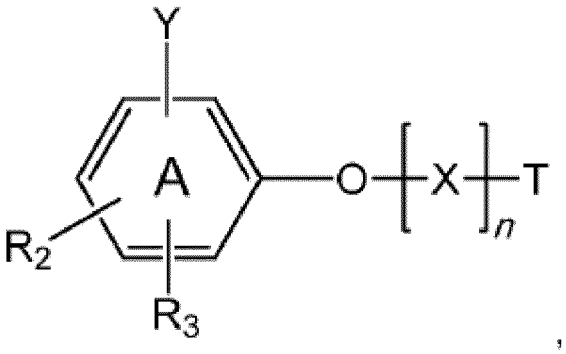
(i) Behandeln eines Textils mit einer wässrigen Lösung des alkoxylierten substituierten Phenol-Dispergiermittels, wobei die wässrige Lösung von 10 ppm bis 5000 ppm des alkoxylierten substituierten Phenol-Dispergiermittels, wie in irgendeinem der vorhergehenden Ansprüche definiert, und 0 bis 6 g/l eines Tensids, ausgenommen das alkoxylierte substituierte Phenol-Dispergiermittel, umfasst; und
(ii) optional Abspülen und Trocknen des Textils.

15. Häusliches Verfahren zum Behandeln eines Textils nach Anspruch 14, wobei bei dem Verfahren die Konzentration des Parfüms in der wässrigen Lösung vorzugsweise von 0,1 bis 100 ppm beträgt.

Revendications

1. Composition de détergent de lessive comprenant :

(i) de 0,5 à 20 % en masse d'un dispersant de phénol substitué alcoxylé de la structure suivante :



dans laquelle

X est choisi parmi : un groupe éthoxy ; et, des mélanges de groupes éthoxy et propoxy où le nombre de groupes éthoxy est supérieur au nombre de groupes propoxy, et dans laquelle n est de 6 à 70 ;
Y est choisi parmi : R_1 ; OR_1, $COOR_5$; F ; Cl ; Br ; I ; CN ; et NO_2, dans laquelle R_1 est un groupe alkyle

linéaire ou ramifié en C1 à C4 et R_5 est choisi parmi des groupes alkyle linéaires ou ramifiés en C1 à C18 ; R_2 et R_3 sont choisis parmi : des groupes alkylaryle linéaires ou ramifiés en C1 à C3 ; et, des groupes aryle ; T est choisi parmi : H ; CH_3 ; SO_3^- ; CH_2COO^- ; PO_3^{2-} ; C_2H_5 ; n-propyle, i-propyle ; n-butyle ; t-butyle ; et, sulfosuccinate ;

(ii) de 0 à 50 % en masse de tensioactif, différent du phénol substitué alcoxylé ; et,
(iii) un actif choisi parmi un ou plusieurs des suivants : de 0,001 à 3 % en masse de parfum ; de 0,0001 à 0,5 % en masse d'un agent fluorescent et/ou de 0,0001 % en masse à 0,1 % en masse de colorant de nuançage.

2. Composition de détergent de lessive selon la revendication 1, dans laquelle R_2 et R_3 sont choisis parmi un groupe styryle et cumyle.

3. Composition de détergent de lessive selon la revendication 1, dans laquelle R_2 et R_3 sont un groupe styryle et à la fois R_2 et R_3 sont dans la position ortho par rapport au groupe $-O-[X]_n-T$.

4. Composition de détergent de lessive selon la revendication 1, 2 ou 3, dans laquelle X est un groupe éthoxy.

5. Composition de détergent de lessive selon l'une quelconque des revendications précédentes, dans laquelle n est de 8 à 34.

6. Composition de détergent de lessive selon l'une quelconque des revendications précédentes, dans laquelle le tensioactif est choisi parmi : des tensioactifs anioniques et non-ioniques et la teneur en tensioactif est de 4 à 40 % en masse.

7. Composition de détergent de lessive selon l'une quelconque des revendications précédentes, dans laquelle la fraction massique de tensioactif non-ionique/tensioactif anionique est de 0 à 0,3.

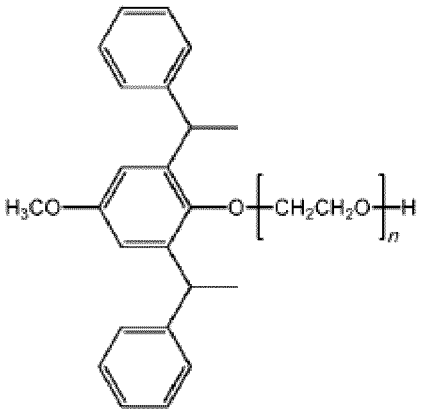
8. Composition de détergent de lessive selon la revendication 6 ou 7, dans laquelle le tensioactif anionique est choisi parmi : des benzènesulfonates d'alkyle linéaires ; des sulfates d'alkyle ; et, des sulfates d'alkyléthers ; et des mélanges de ceux-ci.

9. Composition de détergent de lessive selon l'une quelconque des revendications précédentes, dans laquelle la teneur du dispersant de phénol substitué alcoxylé est de 1 à 10 % en masse.

10. Composition de détergent de lessive selon l'une quelconque des revendications précédentes, dans laquelle T est H.

11. Composition de détergent de lessive selon l'une quelconque des revendications précédentes, dans laquelle le Y est choisi parmi : un groupe méthyle ; éthyle ; méthoxy ; et, éthoxy.

12. Composition de détergent de lessive selon la revendication 1, dans laquelle le dispersant de phénol substitué alcoxylé est :



13. Composition de détergent de lessive selon l'une quelconque des revendications précédentes, dans laquelle n est

choisi parmi : 14 ; 15 ; 16 ; 17 ; 18 ; 19 ; 20 ; 21 ; 22 ; 23 ; 24 ; 25 ; 26 ; 27 ; 28 ; 29 ; 30 ; 31 ; et, 32.

14. Procédé domestique de traitement d'un textile, le procédé comprenant les étapes de :

(i) traitement d'un textile avec une solution aqueuse du dispersant de phénol substitué alcoxylé la solution aqueuse comprenant de 10 ppm à 5 000 ppm du dispersant de phénol substitué alcoxylé selon l'une quelconque des revendications précédentes ; et, de 0 à 6 g/L d'un tensioactif, différent du dispersant de phénol substitué alcoxylé ; et,
(ii) rinçage éventuel et séchage du textile.

15. Procédé domestique de traitement d'un textile selon la revendication 14, dans lequel dans le procédé la teneur du parfum dans la solution aqueuse est de préférence de 0,1 à 100 ppm.

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