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(11)

EP 2 899 259 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
29.07.2015 Bulletin 2015/31

(51) Int Cl.:
C11D 3/37 (2006.01) **C11D 3/42** (2006.01)
C11D 11/02 (2006.01) **C11D 11/00** (2006.01)

(21) Application number: **14152209.4**

(22) Date of filing: **22.01.2014**

(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**
Designated Extension States:
BA ME

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(54) **Detergent compositions**

(57) A composition comprising an amphiphilic graft copolymer and an optical brightener and a process of making a granular detergent composition comprising the steps of:

- a) forming an aqueous detergent slurry;
- b) spray drying said aqueous detergent slurry to form a

plurality of spray-dried detergent particles; and
c) forming an emulsion comprising a surfactant, an amphiphilic graft co-polymer and an optical brightener having ClogP from 1 to 50;
d) adding the emulsion from step c) to at least a portion of said plurality of spray-dried detergent particles.

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Description

FIELD OF THE INVENTION

5 **[0001]** The present invention is directed to compositions comprising optical brightener and polymer and to methods of making granular detergent compositions containing optical brighteners and polymer.

BACKGROUND OF THE INVENTION

10 **[0002]** Consumers may associate the cleaning power of a granular detergent composition with its appearance. For this reason, it may be disadvantageous to market a detergent in which some or all of the granules are discolored. Furthermore, it is also desirable to incorporate optical brighteners into detergent compositions. However, as described in EP686691B formulating certain brighteners through powder formulations does not allow to obtain the required out-

15 **[0003]** Thus, there is a need in the art for a detergent composition that is suited for producing effective fabric whitening. And in the context of granular detergents a need for more consumer acceptable appearance, i.e. non-discoloured granules of consumer-accepted size.

20 **[0004]** The Inventors have found that if the optical brightener is used in combination with an amphiphilic graft copolymer (AGP), optimal performance of the brightener results. In particular if an emulsion or pre-mix is firstly made of the optical brightener with the polymer, this can be sprayed onto the spray-dried particles, and that a granular detergent composition is produced which maximizes performance of the optical brightener and produces granular detergent having a consumer-acceptable appearance.

SUMMARY OF THE INVENTION

25 **[0005]** The present invention addresses the aforementioned needs by providing a detergent composition comprising from 0.0001 to 10 wt% of an optical brightener having a ClogP from 1 to 50 and from 0.05 to 10 wt% of an amphiphilic graft copolymer.

30 **[0006]** The invention also provides a method of making a granular detergent composition comprising the steps of: a) forming an aqueous detergent slurry; b) spray drying said aqueous detergent slurry to form a plurality of spray-dried detergent particles; c) forming an emulsion comprising a surfactant, an optical brightener having ClogP from 1 to 50 and an amphiphilic graft co-polymer; and d) adding the emulsion from step c) to at least a portion of said plurality of spray-dried detergent particles.

DETAILED DESCRIPTION OF THE INVENTION

[0007] As used herein, "consisting essentially of" means that the composition or component may include additional ingredients, but only if the additional ingredients do not materially alter the basic and novel characteristics of the claimed compositions or methods.

40 **[0008]** All percentages, parts and ratios are based upon the total weight of the composition of the present invention and all measurements made are at 25°C, unless otherwise specified. All such weights as they pertain to listed ingredients are based on the active level and therefore do not include carriers or by-products that may be included in commercially available materials, unless otherwise specified.

45 **[0009]** Granular laundry detergents may be manufactured using a spray drying process. The spray drying process typically includes spraying an aqueous slurry comprising detergent ingredients into a spray-drying tower through which hot air flows. As it falls through the tower, the aqueous slurry forms droplets, the hot air causes water to evaporate from the droplets, and a plurality of spray-dried granules is formed. The resulting granules may form the finished granular detergent composition. Alternatively, the resulting granules may be further processed (such as via agglomeration) and/or further components (such as detergent adjuncts) may be added thereto.

Process of making

[0010] The process of the present invention can be batch, continuous, or semi-continuous.

55 **Step a):** an aqueous slurry is prepared using any suitable method. For example, the aqueous slurry may be prepared by mixing detergent ingredients together in a crutcher mixer. The aqueous slurry preferably comprises detergent surfactant, alkalinity source, at least one additional detergent ingredient or a combination thereof. The aqueous slurry may contain water at a weight percentage of from about 25 wt% to about 50 wt%.

The aqueous slurry can comprise from above 0 wt% to about 30 wt% deterative surfactant, preferably from about 10 wt% to about 20 wt% deterative surfactant.

Useful amounts of an alkalinity source can include from about 1 to about 20% or from about 1 to about 10% of alkalinity source by weight of the composition.

The deterative surfactant, alkalinity source and at least one additional detergent ingredient are described in more detail below.

Step b): the aqueous slurry is spray dried using standard techniques. The aqueous slurry is transferred from the mixer preferably through at least a first pump and a second pump to a spray nozzle. Typically, the aqueous slurry is transferred in a pipe. The aqueous slurry is typically transferred through an intermediate storage vessel such as a drop tank, for example when the process is semi-continuous. Alternatively, the process can be a continuous process, in which case no intermediate storage vessel is required. Typically, when two or more pumps are used, the first pump is a low pressure pump, such as a pump that is capable of generating a pressure of from 3×10^5 to 1×10^6 Pa, and the second pump is a high pressure pump, such as a pump that is capable of generating a pressure of from 2×10^6 to 1×10^7 Pa. Optionally, the aqueous slurry is transferred through a disintegrator, such as disintegrators supplied by Hosakawa Micron. The disintegrator can be positioned before the pump, or after the pump. If two or more pumps are present, then the disintegrator can also be positioned between the pumps. Typically, the pumps, disintegrators, intermediate storage vessels, if present, are all in series configuration. However, some equipment may be in a parallel configuration. A suitable spray nozzle is a Spray Systems T4 Nozzle. Gas may be injected into the aqueous slurry at any point after the crutcher mixer and prior to being spray-dried. Further detergent ingredients may also be injected into the aqueous slurry after the crutcher mixer and prior to being spray-dried. For example an liquid anionic surfactant mix may be added to the aqueous slurry after the crutcher mixer and prior to being spray-dried.

The aqueous slurry is sprayed through the spray nozzle into a spray-drying tower. Preferably, the mixture is at a temperature of from 60°C to 140°C when it is sprayed through the spray nozzle into a spray-drying tower. Suitable spray-drying towers are co-current or countercurrent spray-drying towers. The mixture is typically sprayed at a pressure of from 6×10^6 Pa to 1×10^7 Pa. The slurry is spray-dried to form a spray-dried powder. Preferably, the exhaust air temperature is in the range of from 60°C to 100°C.

Step c): an emulsion comprising a surfactant, the optical brightener and the amphiphilic graft co-polymer is prepared. Preferably, the continuous phase of the emulsion comprises the surfactant and the discrete phase comprises the amphiphilic graft co-polymer and preferably also the brightener. The emulsion can be prepared via any suitable method, using any suitable equipment. A preferred method for preparing the emulsion comprises the steps;

- i. forming a first liquid comprising a surfactant;
- ii. forming a second liquid comprising the amphiphilic graft co-polymer;
- iii. incorporating the optical brightener into either the first or second liquid, preferably the second liquid;
- iv. passing the first and second liquids through a mixer; thereby
- v. mixing the first and second liquids to form the emulsion.

Any suitable mixing device can be used. A preferred mixing device is a high shear mixer. Suitable high shear mixers can be dynamic or static mixers. A suitable dynamic mixer can be a rotor-stator mixer. The mixing process can be a batch or continuous process. The liquids may be at a temperature of between room temperature or from 40 °C or from 55 to 65°C as it is added to the mixer. The surfactant may be at a temperature of between room temperature or 35, and 50°C as it is added to the mixer. The temperature of the mixture in the mixer can be between 25, or 40 and 60°C.

The surfactant in the emulsion can be any surfactant, for example, non-ionic, cationic, anionic, zwitterionic or a combination thereof. Preferably, the surfactant in the emulsion is a non-ionic surfactant.

Step d): the emulsion from step c) is added to at least a portion of said plurality of spray-dried detergent particles. The spray-dried particles may be present in a rotary mix drum, or a batch drum or a belt conveyer. The emulsion may be transferred along a pipe to a suitable means for adding the emulsion to at least a portion of said plurality of spray-dried detergent particles. A suitable means of adding could be a spray nozzle. Preferably the emulsion is maintained at a temperature of between 30 and 60°C, preferably between 40 and 60°C prior to addition to the spray-dried detergent particles. This temperature is preferred because at lower temperatures, the viscosity of the emulsion increases. At lower viscosities it is easier to spray the emulsion.

[0011] Without wishing to be bound by theory, it is believed that the addition of the optical brightener in combination with the amphiphilic graft polymer enables better dispersion of the optical brightener as the detergent composition contacts the wash water, leading to increased performance of the optical brightener.

Amphiphilic Graft Copolymer (AGP)

[0012] AGP(s) of use in the present invention are obtainable by grafting a polyalkylene oxide of number average molecular weight from about 2,000 to about 100,000 with vinyl acetate, which may be partially saponified, in a weight ratio of polyalkylene oxide to vinyl acetate of about 1:0.2 to about 1:10. The vinyl acetate may, for example, be saponified to an extent of up to 15%. The polyalkylene oxide may contain units of ethylene oxide, propylene oxide and/or butylene oxide. Selected embodiments comprise ethylene oxide.

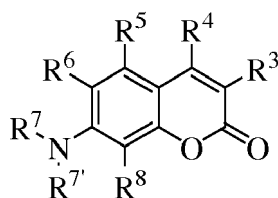
[0013] In some embodiments the polyalkylene oxide has a number average molecular weight of from about 4,000 to about 50,000, and the weight ratio of polyalkylene oxide to vinyl acetate is from about 1:0.5 to about 1:6. A material within this definition, based on polyethylene oxide of molecular weight 6,000 (equivalent to 136 ethylene oxide units), containing approximately 3 parts by weight of vinyl acetate units per 1 part by weight of polyethylene oxide, and having itself a molecular weight of about 24,000, is commercially available from BASF as Sokalan™ HP22. HP22 is a preferred AGP as it provides improved grease stain removal from fabrics during the wash. Selected embodiments of the AGP(s) of use in the present invention as well as methods of making them are described in detail in PCT Patent Application No. WO 2007/138054. They may be present in the granular detergent compositions of the present invention at weight percentages from about 0 to about 5%, from about 0% to about 4%, or from about 0.5% to about 2%. In some embodiments, the AGP(s) is present at greater than about 1.5%. The AGP(s) are found to provide excellent hydrophobic soil suspension even in the presence of cationic coacervating polymers.

[0014] The AGP(s) are based on water-soluble polyalkylene oxides as a graft base and side chains formed by polymerization of a vinyl ester component. These polymers having an average of less than or equal to one graft site per 50 alkylene oxide units and mean molar masses (M_w) of from about 3000 to about 100,000.

The Optical Brightener

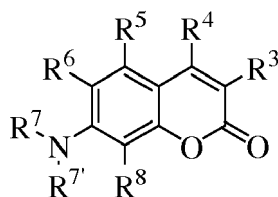
[0015] The optical brightener typically has a ClogP of 1 to 50 (herein, high ClogP), or 2 to 50, or 2.5 to 50, or 3 to 50 or up to 40 or 30 or 20 or up to 10. ClogP is calculated using Advanced Chemistry Development Software V11.02 (© 1994-2012 ACD/Labs), Advanced Chemistry Development, Inc., 8 King Street East, Suite 107, Toronto, Ontario, Canada M5C 1B5. The optical brightener preferably has an extinction co-efficient at the maximum absorbance between 400 and 750nm of less than 1000L/mol cm.

[0016] Preferred optical brighteners include coumarinic and benzoxazole brighteners or mixtures thereof. Coumarinic optical brighteners are particularly preferred. A preferred brightener is selected from coumarinic compounds of Formula I



Formula I

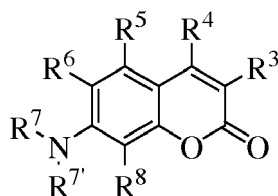
wherein R^3 is selected from the group consisting of H, C1-C4 alkyl, and C6-C10 aromatic or heteroaromatic groups which may be substituted with -F, -Cl, -Br, phenyl and C1-C4 alkyl; R^4 is selected from the group consisting of H, C1-C4 alkyl optionally substituted by OH or $(OCH_2CHR^9)_xOH$ wherein each R^9 is independently selected from H, methyl, and ethyl and x is 1 to 20; R^5 is H, R^6 and R^8 are selected from H and C2-C4 alkylene that combine with one of more of R^7 and $R^{7'}$ to form a heterocyclic ring; R^7 and $R^{7'}$ are selected from the group consisting of H and organic groups that have mass less than 350 Daltons, wherein R^7 and $R^{7'}$ may combine with one another to form a heterocyclic ring; and wherein the weight of the brightener is from 160 to no more than 1400 Daltons, and mixtures thereof. Preferred optical brightener for use in the present invention may be selected from compounds of Formula I



Formula I

wherein R^3 is selected from the group consisting of H, methyl, phenyl optionally substituted with -Cl or C1-C4 alkyl, preferably methyl, triazole optionally substituted with phenyl or C1 - C4 alkyl, and pyrazole optionally substituted with phenyl; R^4 is selected from the group consisting of H, methyl and ethyl optionally substituted by OH or $(OCH_2CHR^9)_x$ OH wherein each R^9 is independently selected from H and methyl, and x is 1 to 10; R^5 , R^6 and R^8 are H; R^7 and $R^{7'}$ are selected from the group consisting of H and organic groups that have mass less than 350 Daltons, wherein R^7 and $R^{7'}$ may combine with one another to form a heterocyclic ring, and mixtures thereof.

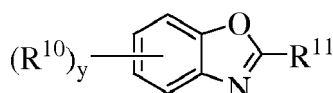
[0017] A preferred optical brightener for use in the present invention may be selected from compounds of Formula I



Formula I

wherein R^3 is selected from the group consisting of H, methyl, and phenyl; R^4 is selected from the group consisting of H and methyl; R^5 , R^6 and R^8 are H; R^7 and $R^{7'}$ are selected from the group consisting of H, C1-C12 branched or unbranched alkyl, and $(CH_2CHR^9O)_xH$ where each R^9 is independently selected from H, methyl, and ethyl and x is 1 to 20, and mixtures thereof.

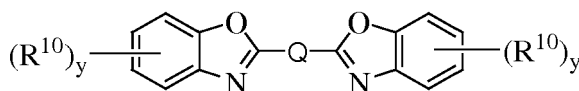
[0018] A preferred optical brightener for use in the present invention may be selected from benzoxazole compounds of Formula II



Formula II

wherein the index y is 1 or 2 and each R^{10} is independently selected from the group consisting of H, -F, -Cl, -Br, C1-C10 alkyl optionally substituted with halo, C6-C10 aryl, C7-C10 alkaryl, $-G_z-N(R^{12})_2$ where z is 0 or 1 and G is selected from the group consisting of C(O) and SO₂ and each R^{12} is independently selected from H, C1-C4 alkyl and $(CH_2CHR^9O)_xH$, and C1-C4 alkyl optionally substituted by OH or $(OCH_2CHR^9)_xOH$, wherein each R^9 is independently selected from H, methyl, and ethyl and x is 1 to 20; R^{11} is selected from the group consisting of aromatic and heteroaromatic organic groups having no carboxylic acid or sulfonic acid groups and weighing less than 400 Daltons.

[0019] Preferred optical brightener for use in the present invention may be selected from compounds of Formula III



Formula III

wherein each index y is independently selected from 1 or 2 and each R^{10} is independently selected from the group consisting of H, -F, -Cl, -Br, C1-C10 alkyl optionally substituted with halo, C6-C10 aryl, C7-C10 alkaryl, $-G_zN(R^{12})_2$ where z is 0 or 1 and G is selected from the group consisting of C(O) and SO₂ and each R^{12} is independently selected from

H, C1-C4 alkyl and $(\text{CH}_2\text{CHR}^9\text{O})_x\text{H}$, and C1-C4 alkyl optionally substituted by OH or $(\text{OCH}_2\text{CHR}^9)_x\text{OH}$, wherein each R^9 is independently selected from H, methyl, and ethyl and x is 1 to 20; Q is a divalent moiety weighing less than 400 Daltons comprising an aromatic or heteroaromatic group and preferably having no carboxylic acid or sulfonic acid groups and weighing less than 400 Daltons.

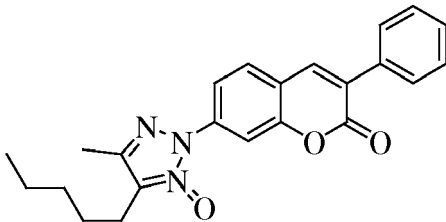
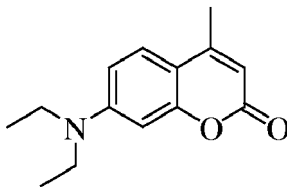
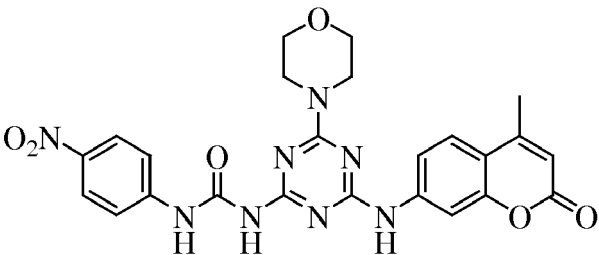
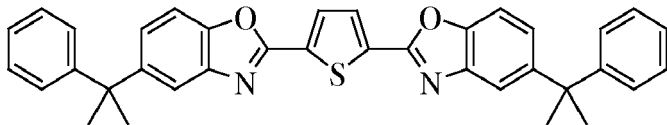
[0020] Suitable Q groups in Formula III include, but are not limited to, 1,4-naphthalene, 1,7-naphthalene, 4,4'-terphenylene, 2,7-dihydro[9,10]phenanthrene, 2,5-thiophene, 4-methyl-2,5-oxazole, 2,5-1,3,4-thiadiazole, 4,4'-(1,2,3-triazol-2-yl)phenyl, 2,6-thieno[3,2-b]benzothiophene, 2,4'-(1,3,4-oxadiazol-5-yl)phenyl, and mixtures thereof.

[0021] Typically the optical brightener is present in the composition in an amount from 1ppb to 10 wt% of the composition. The composition may be a pre-treatment composition for applying directly to an oily stain prior to an aqueous wash or rinse step or it may be provided by combining a detergent composition with water to form a wash liquor. Thus the concentration may vary widely depending on the form of application. Thus the optical brightener may be present in amounts from 1ppb to 50ppm in a wash liquor/solution, preferably from 100ppb or 500ppb to 35ppm. In a pre-treatment composition or detergent composition for dilution, more usually in an amount from 0.00001 to 10 wt%, or from 0.0001 or 0.01 or even from 0.05 to 5 or 2 wt% of the pre-treat or detergent composition.

[0022] The optical brightener may be incorporated into the detergent composition by first forming a pre-mix comprising the optical brightener, for example where the pre-mix comprises a particle or concentrated liquid for incorporation into the composition, it may be preferred that the optical brightener is present at a level of from 0.001 or even 0.01 to 10 wt% of the pre-mix.

[0023] Examples of preferred brighteners are shown in Table 1.

Table 1: Optical brighteners

No.	Formula
Example 1	 7-(4-methyl-1-oxido-5-pentyl-2H-1,2,3-triazol-2-yl)-3-phenyl-2H-1-benzopyran-2-one
Example 2	 7-(diethylamino)-4-methyl-2H-1-benzopyran-2-one
Example 3	 N-[4-[(4-methyl-2-oxo-2H-1-benzopyran-7-yl)amino]-6-(4-morpholinyl)-1,3,5-triazin-2-yl]-N'-(4-nitrophenyl)urea
Example 4	 2,2'-(2,5-thiophenediyl)bis[5-(1-methyl-1-phenylethyl)benzoxazole]

(continued)

No.	Formula
Example 5	2,2'-(2,5-thiophenediyl)bis[5-(1,1,3,3-tetramethylbutyl)benzoxazole]
Example 6	

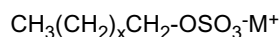
Deterstive Surfactant

[0024] Any suitable deterstive surfactant is of use in the aqueous slurry.

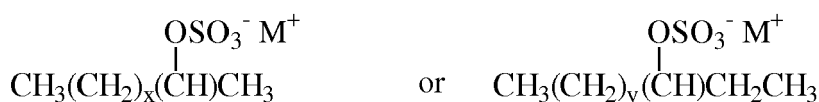
[0025] Suitable deterstive surfactants include, but are not limited to: anionic surfactants, non-ionic surfactants, cationic surfactants, zwitterionic surfactants, amphoteric surfactants and any mixtures thereof. Preferred surfactants include anionic surfactants, cationic surfactants, non-ionic surfactants and any mixtures thereof.

[0026] Suitable anionic surfactants can include alkyl benzene sulphonate. Preferably the anionic deterstive surfactant comprises at least 50 wt%, at least 55 wt%, at least 60 wt%, at least 65 wt%, at least 70 wt%, at least 75 wt%, at least 80 wt%, at least 85 wt%, at least 90 wt%, or even at least 95 wt%, by weight of the anionic deterstive surfactant, of alkyl benzene sulphonate. The alkyl benzene sulphonate is preferably a linear or branched, substituted or unsubstituted, C₈₋₁₈ alkyl benzene sulphonate. This is the optimal level of the C₈₋₁₈ alkyl benzene sulphonate to provide a good cleaning performance. The C₈₋₁₈ alkyl benzene sulphonate can be a modified alkylbenzene sulphonate (MLAS) as described in more detail in WO 99/05243, WO 99/05242, WO 99/05244, WO 99/05082, WO 99/05084, WO 99/05241, WO 99/07656, WO 00/23549, and WO 00/23548. Highly preferred C₈₋₁₈ alkyl benzene sulphonates are linear C₁₀₋₁₃ alkylbenzene sulphonates. Especially preferred are linear C₁₀₋₁₃ alkylbenzene sulphonates that are obtainable by sulphonating commercially available linear alkyl benzenes (LAB); suitable LAB include low 2-phenyl LAB, such as those supplied by Sasol under the trade name Isochem[®] or those supplied by Petresa under the trade name Petrelab[®]. Other suitable LAB include high 2-phenyl LAB, such as those supplied by Sasol under the trade name Hyblene[®].

[0027] The anionic deterstive surfactant may preferably comprise other anionic deterstive surfactants. A suitable anionic deterstive surfactant is a non-alkoxylated anionic deterstive surfactant. The non-alkoxylated anionic deterstive surfactant can be an alkyl sulphate, an alkyl phosphate, an alkyl phosphonate, an alkyl carboxylate or any mixture thereof. The non-alkoxylated anionic surfactant can be selected from the group consisting of; C₁₀-C₂₀ primary, branched-chain, linear-chain and random-chain alkyl sulphates (AS), typically having the following formula (I):



wherein, M is hydrogen or a cation which provides charge neutrality, preferred cations are sodium and ammonium cations, wherein x is an integer of at least 7, preferably at least 9; C₁₀-C₁₈ secondary (2,3) alkyl sulphates, typically having the following formulae:



wherein, M is hydrogen or a cation which provides charge neutrality, preferred cations include sodium and ammonium cations, wherein x is an integer of at least 7, preferably at least 9, y is an integer of at least 8, preferably at least 9; C₁₀-C₁₈ alkyl carboxylates; mid-chain branched alkyl sulphates as described in more detail in US 6,020,303 and US

6,060,443; methyl ester sulphonate (MES); alpha-olefin sulphonate (AOS); and mixtures thereof.

[0028] Another preferred anionic deterative surfactant is an alkoxyated anionic deterative surfactant. The presence of an alkoxyated anionic deterative surfactant in the spray-dried powder provides good greasy soil cleaning performance, gives a good sudsing profile, and improves the hardness tolerance of the anionic deterative surfactant system. It may be preferred for the anionic deterative surfactant to comprise from 1% to 50%, or from 5%, or from 10%, or from 15%, or from 20%, and to 45%, or to 40%, or to 35%, or to 30%, by weight of the anionic deterative surfactant system, of an alkoxyated anionic deterative surfactant.

[0029] Preferably, the alkoxyated anionic deterative surfactant is a linear or branched, substituted or unsubstituted C₁₂₋₁₈ alkyl alkoxyated sulphate having an average degree of alkoxylation of from 0.5 to 30, preferably from 0.5 to 10, more preferably from 0.5 to 3. Preferably, the alkoxyated anionic deterative surfactant is a linear or branched, substituted or unsubstituted C₁₂₋₁₈ alkyl ethoxyated sulphate having an average degree of ethoxylation of from 0.5 to 10, more preferably from 0.5 to 3. Most preferably, the alkoxyated anionic deterative surfactant is a linear unsubstituted C₁₂₋₁₈ alkyl ethoxyated sulphate having an average degree of ethoxylation of from 0.5 to 7, more preferably from 0.5 to 3.

[0030] The alkoxyated anionic deterative surfactant, when present with an alkyl benzene sulphonate may also increase the activity of the alkyl benzene sulphonate by making the alkyl benzene sulphonate less likely to precipitate out of solution in the presence of free calcium cations. Preferably, the weight ratio of the alkyl benzene sulphonate to the alkoxyated anionic deterative surfactant is in the range of from 1:1 to less than 5:1, or to less than 3:1, or to less than 1.7:1, or even less than 1.5:1. This ratio gives optimal whiteness maintenance performance combined with a good hardness tolerance profile and a good sudsing profile. However, it may be preferred that the weight ratio of the alkyl benzene sulphonate to the alkoxyated anionic deterative surfactant is greater than 5:1, or greater than 6:1, or greater than 7:1, or even greater than 10:1. This ratio gives optimal greasy soil cleaning performance combined with a good hardness tolerance profile, and a good sudsing profile.

[0031] Suitable alkoxyated anionic deterative surfactants are: Texapan LEST™ by Cognis; Cosmacol AES™ by Sasol; BES151™ by Stephan; Empicol ESC70/U™; and mixtures thereof.

[0032] Preferably, the anionic deterative surfactant comprises from 0% to 10%, preferably to 8%, or to 6%, or to 4%, or to 2%, or even to 1%, by weight of the anionic deterative surfactant, of unsaturated anionic deterative surfactants such as alpha-olefin sulphonate. Preferably the anionic deterative surfactant is essentially free of unsaturated anionic deterative surfactants such as alpha-olefin sulphonate. By "essentially free of" it is typically meant "comprises no deliberately added". Without wishing to be bound by theory, it is believed that these levels of unsaturated anionic deterative surfactants such as alpha-olefin sulphonate ensure that the anionic deterative surfactant is bleach compatible.

[0033] Preferably, the anionic deterative surfactant comprises from 0% to 10%, preferably to 8%, or to 6%, or to 4%, or to 2%, or even to 1%, by weight of alkyl sulphate. Preferably the anionic deterative surfactant is essentially free of alkyl sulphate. Without wishing to be bound by theory, it is believed that these levels of alkyl sulphate ensure that the anionic deterative surfactant is hardness tolerant.

[0034] Suitable non-ionic deterative surfactant can be selected from the group of: C₈-C₁₈ alkyl ethoxylates, such as, NEODOL® non-ionic surfactants from Shell; C₆-C₁₂ alkyl phenol alkoxyates wherein the alkoxyate units are ethyleneoxy units, propyleneoxy units or a mixture thereof; C₁₂-C₁₈ alcohol and C₆-C₁₂ alkyl phenol condensates with ethylene oxide/propylene oxide block polymers such as Pluronic® from BASF; C₁₄-C₂₂ mid-chain branched alcohols, BA, as described in more detail in US 6,150,322; C₁₄-C₂₂ mid-chain branched alkyl alkoxyates, BAEx, wherein x = from 1 to 30, as described in more detail in US 6,153,577, US 6,020,303 and US 6,093,856; alkylpolysaccharides as described in more detail in US 4,565,647, specifically alkylpolyglycosides as described in more detail in US 4,483,780 and US 4,483,779; polyhydroxy fatty acid amides as described in more detail in US 5,332,528, WO 92/06162, WO 93/19146, WO 93/19038, and WO 94/09099; ether capped poly(oxyalkylated) alcohol surfactants as described in more detail in US 6,482,994 and WO 01/42408; and mixtures thereof.

[0035] The non-ionic deterative surfactant could be an alkyl polyglucoside and/or an alkyl alkoxyated alcohol. Preferably the non-ionic deterative surfactant is a linear or branched, substituted or unsubstituted C₈₋₁₈ alkyl ethoxyated alcohol having an average degree of ethoxylation of from 1 to 10, more preferably from 3 to 7.

Alkalinity Source

[0036] Any suitable alkalinity source is of use in the aqueous slurry. Suitable alkalinity sources include, but are not limited to being selected from the group of: carbonate salt; silicate salt; sodium hydroxide; and mixtures thereof. Exemplary alkalinity sources may be selected from the group of: sodium carbonate; sodium silicate; and mixtures thereof.

Additional Detergent Ingredients

[0037] The additional detergent ingredient may include a builder. Any suitable builder may be of use in the aqueous slurry. Suitable builders include, but are not limited to those selected from the group of: zeolite builder; phosphate builder;

and mixtures thereof. Non-limiting examples of useful zeolite builders include: zeolite A; zeolite X; zeolite P; zeolite MAP; and combinations thereof. Sodium tripolyphosphate is a non-limiting example of a useful phosphate builder. The zeolite builder(s) may be present at from about 1 to about 20 % by weight of the detergent composition. It may also be especially preferred for the granular detergent composition to comprise low levels, or even be essentially free, of builder. By

essentially free of it is typically meant herein to mean: "comprises no deliberately added". In a preferred embodiment, the granular detergent composition is essentially free of zeolite, preferably has no zeolite. In a preferred embodiment, the granular detergent composition is essentially free of phosphate, preferably has no phosphate.

[0038] The additional detergent ingredient may include a polymer. Any suitable polymer may be of use in the aqueous slurry. Suitable polymers include, but are not limited to: polymeric carboxylate; polyester soil release agent; cellulosic polymer; and mixtures thereof. One preferred polymeric material is a polymeric carboxylate, such as a co-polymer of maleic acid and acrylic acid. However, other polymers may also be suitable, such as polyamines (including the ethoxylated variants thereof), polyethylene glycol and polyesters. Polymeric soil suspending aids and polymeric soil release agents are also particularly suitable.

[0039] Another suitable polymer is cellulosic polymer, such as cellulosic polymer selected from the group of: alkyl alkoxy cellulose, preferably methyl hydroxyethyl cellulose (MHEC); alkyl cellulose, preferably methyl cellulose (MC); carboxy alkyl cellulose, preferably carboxymethylcellulose (CMC); and mixtures thereof.

[0040] Polymers may be present at from about 0.5 to about 20% or from about 1 to about 10% by weight of the detergent composition.

[0041] Other suitable detergent ingredients may be selected from the group of: chelants such as ethylene diamine disuccinic acid (EDDS); hydroxyethylene diphosphonic acid (HEDP); starch; sodium sulphate; carboxylic acids such as citric acid or salts thereof such as citrate; suds suppressor; fluorescent whitening agent; hueing agent; flocculating agent such as polyethylene oxide; and mixtures thereof. If the present detergent comprises masking agents and/or whiteners (e.g. Titanium dioxide), they may be present at less than about 1 wt% or less.

Emulsion

[0042] The emulsion comprises a surfactant continuous phase and an amphiphilic graft copolymer (AGP) discrete phase. Thus, the surfactant and the AGP are immiscible with other. Preferably, the surfactant is water-soluble and independently the AGP is water-soluble. Most preferably, the surfactant and the AGP are water-soluble. Preferably, the graft co-polymer has a viscosity of up to 4Pa.s at 55°C, or even up to 3Pa.s. The viscosity is typically measured using a rheometer at a shear of 100s⁻¹ and a temperature of 70°C. Those skilled in the art will recognize suitable apparatus in order to measure the viscosity. An exemplary method is to measure the viscosity at a shear rate of 100s⁻¹ at temperature of 70°C, using a TA AR 2000ex, controlled stress rheometer, using a TA Instruments Peltier Concentric Cylinder Conical DIN System, hard anodized Aluminium cup and rotor, having a rotor radius of 14mm, a rotor height of 42mm, a cup radius of 15mm, and a sample volume of 19.6ml.

[0043] As detailed above, this viscosity is preferred as it allows more efficient spraying of the emulsion on the spray-dried detergent particles.

[0044] The ratio of surfactant to AGP can be from 1:2 to 2:1.

[0045] The inventors have found that when certain polymers such as amphiphilic graft copolymer(s) (hereinafter "AGP(s)") are spray-dried with other detergent ingredients, the resulting spray-dried powder has a consumer undesirable yellow hue. The yellowing can be especially problematic in detergent matrices having high alkalinity and/or that are processed under high temperature conditions. Without wishing to be bound by theory, it is believed that the discoloration of the granules results from the occurrence of one or more chemical reactions with the AGP(s) as it is subjected to the conditions in the tower. Such reactions may include:

- a. Chain degradation reaction through oxidation may occur at the level of the polymer PEG backbone;
- b. Dehydration of the vinyl acetate/alcohol functionalities can lead to formation of double bonds in the hydrophobic side chains;
- c. Hydrolysis reactions may occur at the vinyl acetate functionalities of the hydrophobic side chains; and/or
- d. Residuals (monomer residue) may form acetaldehyde & acetate.

[0046] The surfactant can be selected from non-ionic, cationic, anionic, zwitterionic surfactants and mixtures thereof. The surfactant may be a non-ionic surfactant, an anionic surfactant or a mixture thereof. The surfactant may be a non-ionic surfactant, or even an alkoxyated non-ionic surfactant. Preferably, the surfactant is anhydrous. This has the benefit of limiting the amount of water that is transferred onto the spray-dried detergent particles. It is most preferred to use a non-ionic anhydrous surfactant as this as a lower viscosity as compared to other anhydrous surfactants. This lower viscosity aids both the emulsification and the process of spraying onto the spray-dried detergent particles. Without being bound by theory, if the viscosity of the continuous phase of the emulsion is too high, then the energy input required to

achieve the emulsion will be very high. This is cost and energy inefficient. Furthermore, if the surfactant viscosity is too high, this can cause blockages of nozzles etc during the making process and higher levels of undesirable oversized particles.

[0047] The non-ionic surfactant for use in the emulsion could be an alkyl polyglucoside and/or an alkyl alkoxyated alcohol. Preferably the non-ionic surfactant is a linear or branched, substituted or unsubstituted C₈₋₁₈ alkyl ethoxylated alcohol having an average degree of ethoxylation of from 1 to 10, more preferably from 3 to 7.

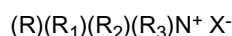
[0048] Suitable non-ionic surfactants include alkyl polyglucoside and/or an alkyl alkoxyated alcohol. Preferred non-ionic alkyl alkoxyated alcohols include C₈₋₁₈ alkyl alkoxyated alcohol, preferably a C₈₋₁₈ alkyl ethoxylated alcohol, preferably the alkyl alkoxyated alcohol has an average degree of alkoxylation of from 1 to 50, preferably from 1 to 30, or from 1 to 20, or from 1 to 10, preferably the alkyl alkoxyated alcohol is a C₈₋₁₈ alkyl ethoxylated alcohol having an average degree of ethoxylation of from 1 to 10, preferably from 1 to 7, more preferably from 1 to 5 and most preferably from 3 to 7. The alkyl alkoxyated alcohol can be linear or branched, and substituted or un-substituted. Suitable non-ionic surfactants can be selected from the group consisting of: C₈₋₁₈ alkyl ethoxylates, such as, NEODOL® non-ionic surfactants from Shell; C₆₋₁₂ alkyl phenol alkoxyates wherein preferably the alkoxyate units are ethyleneoxy units, propyleneoxy units or a mixture thereof; C₁₂₋₁₈ alcohol and C₆₋₁₂ alkyl phenol condensates with ethylene oxide/propylene oxide block polymers such as Pluronic® from BASF; C₁₄₋₂₂ mid-chain branched alcohols; C₁₄₋₂₂ mid-chain branched alkyl alkoxyates, preferably having an average degree of alkoxylation of from 1 to 30; alkylpolysaccharides, preferably alkylpolyglycosides; polyhydroxy fatty acid amides; ether capped poly(oxyalkylated) alcohol surfactants; and mixtures thereof.

[0049] Suitable non-ionic surfactants for use in the emulsion can be selected from the group of: C₈₋₁₈ alkyl ethoxylates, such as, NEODOL® non-ionic surfactants from Shell; C₆₋₁₂ alkyl phenol alkoxyates wherein the alkoxyate units are ethyleneoxy units, propyleneoxy units or a mixture thereof; C₁₂₋₁₈ alcohol and C₆₋₁₂ alkyl phenol condensates with ethylene oxide/propylene oxide block polymers such as Pluronic® from BASF; C₁₄₋₂₂ mid-chain branched alcohols, BA, as described in more detail in US 6,150,322; C₁₄₋₂₂ mid-chain branched alkyl alkoxyates, BAEx, wherein x = from 1 to 30, as described in more detail in US 6,153,577, US 6,020,303 and US 6,093,856; alkylpolysaccharides as described in more detail in US 4,565,647, specifically alkylpolyglycosides as described in more detail in US 4,483,780 and US 4,483,779; polyhydroxy fatty acid amides as described in more detail in US 5,332,528, WO 92/06162, WO 93/19146, WO 93/19038, and WO 94/09099; ether capped poly(oxyalkylated) alcohol surfactants as described in more detail in US 6,482,994 and WO 01/42408; and mixtures thereof.

[0050] Anionic surfactants can include sulphate and sulphonate surfactants. Preferred sulphonate surfactants include alkyl benzene sulphonate, preferably C₁₀₋₁₃ alkyl benzene sulphonate. Suitable alkyl benzene sulphonate (LAS) is obtainable, preferably obtained, by sulphonating commercially available linear alkyl benzene (LAB); suitable LAB includes low 2-phenyl LAB, such as those supplied by Sasol under the tradename Isochem® or those supplied by Petresa under the tradename Petrelab®, other suitable LAB include high 2-phenyl LAB, such as those supplied by Sasol under the tradename Hyblene®. A suitable anionic surfactant is alkyl benzene sulphonate that is obtained by DETAL catalyzed process, although other synthesis routes, such as HF, may also be suitable. Preferred sulphate surfactants include alkyl sulphate, preferably C₈₋₁₈ alkyl sulphate, or predominantly C₁₂ alkyl sulphate. Another preferred sulphate surfactant is alkyl alkoxyated sulphate, preferably alkyl ethoxylated sulphate, preferably a C₈₋₁₈ alkyl alkoxyated sulphate, preferably a C₈₋₁₈ alkyl ethoxylated sulphate, preferably the alkyl alkoxyated sulphate has an average degree of alkoxylation of from 0.5 to 20, preferably from 0.5 to 10, preferably the alkyl alkoxyated sulphate is a C₈₋₁₈ alkyl ethoxylated sulphate having an average degree of ethoxylation of from 0.5 to 10, preferably from 0.5 to 7, more preferably from 0.5 to 5 and most preferably from 0.5 to 3. The alkyl sulphate, alkyl alkoxyated sulphate and alkyl benzene sulphonates may be linear or branched, substituted or un-substituted.

[0051] Suitable organic anionic surfactants include alkyl aryl sulphonates, for example sodium dodecyl benzene sulphonate, long chain (fatty) alcohol sulphates, olefin sulphates and sulphonates, sulphated monoglycerides, sulphated esters, sulphonated or sulphated ethoxylate alcohols, sulphosuccinates, alkane sulphonates, alkali metal soaps of higher fatty acids, phosphate esters, alkyl isethionates, alkyl taurates and/or alkyl sarcosinates.

[0052] Suitable cationic surfactants include alkyl pyridinium compounds, alkyl quaternary ammonium compounds, alkyl quaternary phosphonium compounds, alkyl ternary sulphonium compounds, and mixtures thereof. Preferred cationic surfactants are quaternary ammonium compounds having the general formula:



wherein, R is a linear or branched, substituted or unsubstituted C₆₋₁₈ alkyl or alkenyl moiety, R₁ and R₂ are independently selected from methyl or ethyl moieties, R₃ is a hydroxyl, hydroxymethyl or a hydroxyethyl moiety, X is an anion which provides charge neutrality, preferred anions include: halides, preferably chloride; sulphate; and sulphonate. Preferred cationic deterative surfactants are mono-C₆₋₁₈ alkyl mono-hydroxyethyl di-methyl quaternary ammonium chlorides. Highly preferred cationic deterative surfactants are mono-C₈₋₁₀ alkyl mono-hydroxyethyl di-methyl quaternary ammonium chlo-

ride, mono-C₁₀₋₁₂ alkyl mono-hydroxyethyl di-methyl quaternary ammonium chloride and mono-C₁₀ alkyl mono-hydroxyethyl di-methyl quaternary ammonium chloride.

[0053] A cationic surfactant can for example be an alkylamine salt, a quaternary ammonium salt, a sulphonium salt or a phosphonium salt.

5 **[0054]** A zwitterionic (amphoteric) surfactant can for example be an imidazoline compound, an alkylaminoacid salt or a betaine.

The Detergent Composition

10 **[0055]** The detergent composition is suitable for any laundry detergent application, for example: laundry, including automatic washing machine laundering and hand laundering, and even bleach and laundry additives.

[0056] The detergent composition can be a fully formulated detergent product, such as a fully formulated laundry detergent product, or it can be combined with other particles to form a fully formulated detergent product, such as a fully formulated laundry detergent product. When the detergent composition is a granular detergent composition it may be
15 combined with other particles such as: enzyme particles; perfume particles including agglomerates or extrudates of perfume microcapsules, and perfume encapsulates such as starch encapsulated perfume accord particles; surfactant particles, such as non-ionic detergents surfactant particles including agglomerates or extrudates, anionic detergents surfactant particles including agglomerates and extrudates, and cationic detergents surfactant particles including agglomerates and extrudates; polymer particles including soil release polymer particles, cellulosic polymer particles; buffer particles
20 including carbonate salt and/or silicate salt particles, preferably a particle comprising carbonate salt and silicate salt such as a sodium carbonate and sodium silicate co-particle, and particles and sodium bicarbonate; other spray-dried particles; fluorescent whitening particles; aesthetic particles such as coloured noodles or needles or lamellae particles; bleaching particles such as percarbonate particles, especially coated percarbonate particles, including carbonate and/or sulphate coated percarbonate, silicate coated percarbonate, borosilicate coated percarbonate, sodium perborate coated
25 percarbonate; bleach catalyst particles, such as transition metal catalyst bleach particles, and imine bleach boosting particles; performed peracid particles; hueing dye particles; and any mixture thereof.

[0057] It may also be especially preferred for the granular detergent composition to comprise low levels, or even be essentially free, of builder. By essentially free of it is typically meant herein to mean: "comprises no deliberately added". In a preferred embodiment, the granular detergent composition comprises no builder.

30 **[0058]** The whiteness of the granular detergent composition can be measured using a HunterLab Color difference meter and following appropriate operating procedure. Various models of the HunterLab Color difference meter can be used, such as the HunterLab LabScan XE or HunterLab Model D25. Care is taken to make sure that the powder sample is free of lumps and is representative of the overall particle size. The readings are taken at ambient temperature.

[0059] A HunterLab color difference meter is used to characterize color of a sample into three different parameters according to the Hunter L, a, b color scale. In this scale, the differences between points plotted in a color space correspond to visual differences between the colors plotted. The Hunter L, a, b color scale is organized in cube form. The L axis of the cube runs from top to bottom. The maximum for L is 100, which would be a perfect reflecting diffuser. The minimum for L would be zero, which would be black. The a and b axes of the cube have no specific numerical limits. Positive a is red. Negative a is green. Positive b is yellow. Negative b is blue.

40 **[0060]** The "L-3b" (L minus 3b) value signifies the whiteness of the sample. The whiteness of a blown powder according to the present invention is at least about 73.5.

[0061] The granular detergent composition according to the present invention may have a bulk density of from about 250 to about 550 grams per liter, or from about 300 to about 450 grams per liter.

45 **[0062]** The granular detergent composition may have a mean particle granule size of from about 300 to about 550 microns, or from about 350 to about 450 microns.

EXAMPLES

[0063] A granular laundry detergent composition according to the present invention is prepared.

50 **[0064]** An aqueous alkaline slurry composed of sodium sulphate, sodium carbonate, water, acrylate/maleate co-polymer and miscellaneous ingredients is prepared at 80 °C in a crutcher making vessel. The aqueous slurry is essentially free from zeolite builder and essentially free from phosphate builder. Alkyl benzene sulphonic acid (HLAS) and sodium hydroxide are added to the aqueous slurry and the slurry is pumped through a standard spray system pressure nozzle and atomized into a counter current spray drying tower at an air inlet temperature of 275 °C. The atomized slurry is dried
55 to produce a solid mixture, which is then cooled and sieved to remove oversize material (>1.8mm) to form a spray-dried powder.

[0065] The composition of the spray-dried powder is given Table 1.

Table 1

Component	%w/w Spray Dried Powder
Sodium silicate salt	10.0
C ₈ -C ₂₄ alkyl benzene sulphonate	15.1
Acrylate/maleate copolymer	4.0
Hydroxyethane di(methylene phosphonic acid)	0.7
Sodium carbonate	11.9
Sodium sulphate	53.7
Water	2.5
Miscellaneous, such as magnesium sulphate, and one or more stabilizers	2.1
Total Parts	100.00

Table 2

Component	%w/w granular laundry detergent composition
Spray-dried powder (described above in table 1)	59.38
91.6wt% active linear alkyl benzene sulphonate flake supplied by Stepan under the tradename Nacconol 90G®	0.22
Citric acid	5.00
Sodium percarbonate (having from 12% to 15% active AvOx)	14.70
Photobleach particle	0.01
Lipase (11.00mg active/g)	0.70
Amylase (21.55mg active/g)	0.33
Protease (56.00mg active/g)	0.43
Tetraacetyl ethylene diamine agglomerate (92wt% active)	4.35
Suds suppressor agglomerate (11.5wt% active)	0.87
Acrylate/maleate copolymer particle (95.7wt% active)	0.29
Green/Blue carbonate speckle	0.50
Sodium Sulphate	9.63
Solid perfume particle	0.63
Sokalan HP22 polymer supplied by BASF (72.5 % active polymer)	1.63
Ethoxylated C ₁₂ -C ₁₈ alcohol having an average degree of ethoxylation of 7 (AE7)	1.33
7-(Diethylamino)-4-methyl-2H-chromen-2-one	0.5
Total Parts	100.00

[0066] The granular laundry detergent composition of Table 2 is prepared by dry-mixing all of the above components (all except the AE7, Sokalan HP22 polymer and optical brightener, 7-(Diethylamino)-4-methyl-2H-chromen-2-one) in a continuous rotary mixer (drum diameter 0.6 meters, drum length 1.8 meters, 28 revolutions per min). The total mass flow rate of the powder feeds into the continuous rotary mixer set at 2913 kg/hr. A mixture of AE7 in liquid form and Sokalan HP22 polymer and 7-(Diethylamino)-4-methyl-2H-chromen-2-one in liquid form is sprayed on the particles as they pass through the continuous rotary mixer. The mass flow rate of the liquid mixture is set to 88.9 kg/hr according to

formulation in table 2. The liquid mixture is atomized into droplets by air assisted nozzles operating at a air supply pressure of 5.2 bar gauge prior to liquid mixture addition into the continuous rotary mixer.

[0067] According to the present invention, a granular detergent composition (Granular detergent A) is prepared where the liquid mixture is first emulsified (AE7 continuous phase) by passing through a high shear dynamic mixer (IKA Dispax-Reactor®; Model Size: DR2000/ Mixer Speed 4000 rpm) prior to atomizing and adding to powder.

[0068] The dimensions and values disclosed herein are not to be understood as being strictly limited to the exact numerical values recited. Instead, unless otherwise specified, each such dimension is intended to mean both the recited value and a functionally equivalent range surrounding that value. For example, a dimension disclosed as "40 mm" is intended to mean "about 40 mm."

Claims

1. A liquid or granular detergent composition comprising from 0.0001 to 10 wt% of an optical brightener having a ClogP from 1 to 50 and from 0.05 to 10 wt% of an amphiphilic graft copolymer.
2. A process of making a granular detergent composition comprising the steps of: a) forming an aqueous detergent slurry; b) spray drying said aqueous detergent slurry to form a plurality of spray-dried detergent particles; c) forming an emulsion comprising a surfactant, an optical brightener having ClogP from 1 to 50 and an amphiphilic graft copolymer; and d) adding the emulsion from step c) to at least a portion of said plurality of spray-dried detergent particles.
3. The process according to claim 2, wherein the surfactant is a non-ionic surfactant, preferably an alkyl alkoxylated alcohol having an average degree of alkoxylation of from 1 to 50.
4. The process according to claim 2 or claim 3, wherein the non-ionic surfactant and the amphiphilic graft co-polymer are water-soluble.
5. A composition according to claim 1 or a process according to any of claims 2 to 4, wherein the amphiphilic graft copolymer comprises a graft copolymer of polyethylene, polypropylene or polybutylene oxide with vinyl acetate in a weight ratio of from about 1:0.2 to about 1:10.
6. A composition according to claim 1 or a process according to any of claims 2 to 5 wherein the optical brightener comprises a coumarinic or benzoxazole brightener, preferably a coumarinic brightener.
7. The process according to any of claims 2 to 6, wherein the aqueous detergent slurry comprises a deterative surfactant preferably selected from the group of: alkyl benzene sulfonate; alkoxylated alkyl sulfate; alkyl sulfate; alkoxylated alcohol; and mixtures thereof.
8. The process according to any of claims 2 to 7, wherein the aqueous detergent slurry comprises at least one additional detergent ingredient preferably selected from the group of: polymeric carboxylate; chelant; starch; sodium sulphate; citric acid; cellulosic polymer; suds suppressor; fluorescent whitening agent; hueing agent; flocculating agent; polyester soil release agent; or a mixture thereof.
9. The process according to any of claims 2 to 8, wherein the aqueous detergent slurry comprises an alkalinity source preferably selected from the group of: carbonate salt; silicate salt; sodium hydroxide; and mixtures thereof.
10. The process according to any of claims 2 to 9, wherein said aqueous detergent slurry comprises from 0wt% to 5% zeolite builder and from 0wt% to 5% phosphate builder.
11. The process according to any of claims 2 to 10 claims, wherein the emulsion is at a temperature of from 30°C to 60°C, preferably 40°C to 60°C prior to it being added to the detergent particles.
12. The process according to any of claims 2 to 11 wherein the emulsion is prepared by;
 - i. forming a first liquid comprising a non-ionic surfactant;
 - ii. forming a second liquid comprising an amphiphilic graft co-polymer;
 - iii. incorporating the optical brightener into the first or second liquid;
 - iv. passing the first and second liquids through a high shear mixer;

v. mixing the first and second liquids to form the emulsion.

13. The process according to claim 12, wherein the high shear mixer is a rotor-stator device.

5 **14.** The process according to any preceding claims, wherein the process is continuous.

15. The process according to any preceding claims, wherein the ratio of non-ionic surfactant to amphiphilic graft co-polymer is from 1:2 to 2:1.

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EUROPEAN SEARCH REPORT

 Application Number
 EP 14 15 2209

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