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(71) Applicant: THE PROCTER & GAMBLE COMPANY
[US/US]; One Procter & Gamble Plaza, Cincinnati, Ohio
45202 (US).(72) Inventors: DORGAN, Jill, Robyn; Whitley Road, Long-
benton, Newcastle upon Tyne NE12 9TS (GB). TANTAWY, Hossam, Hassan; Whitley Road, Long-
benton, Newcastle upon Tyne NE12 9TS (GB). PORTER, Adam; Whitley Road, Longbenton, Newcastle upon Tyne
NE12 9TS (GB). CHIEFFI, Andre; Whitley Road, Long-
benton, Newcastle upon Tyne NE12 9TS (GB).
MCMEEKIN, Anthony; Whitley Road, Longbenton,

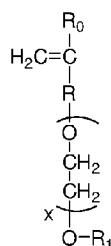
Newcastle upon Tyne NE12 9TS (GB). GOULD, Paul, Anthony; Whitley Road, Longbenton, Newcastle upon Tyne NE12 9TS (GB). CAUFIELD, William, Alexander; Whitley Road, Longbenton, Newcastle upon Tyne NE12 9TS (GB). SMALLEY, Laura, Judith; Whitley Road, Longbenton, Newcastle upon Tyne NE12 9TS (GB). IRVINE, Michael, Richard; Whitley Road, Longbenton, Newcastle upon Tyne NE12 9TS (GB).

(74) Agent: KREBS, Jay A.; c/o The Procter & Gamble Com-
pany, Global Patent Services, One Procter & Gamble
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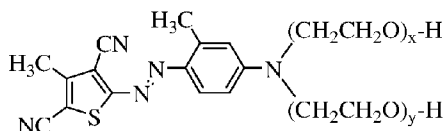
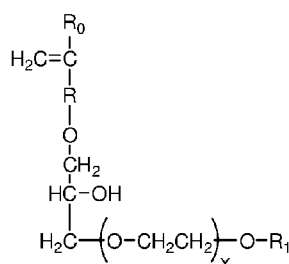
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(54) Title: SOLID FREE-FLOWING PARTICULATE LAUNDRY DETERGENT COMPOSITION

formula (I):



formula (II)



(57) **Abstract:** The present invention relates to a solid free-flowing particulate laundry detergent composition comprising: (a) from 0.1wt% to 5wt% polymer particle comprising: (i) from 70wt% to 90wt% co-polymer, wherein the co-polymer comprises: (i.i) from 50 to less than 98 wt% structural units derived from one or more monomers comprising carboxyl groups; (i.ii) from 1 to less than 49 wt% structural units derived from one or more monomers comprising sulfonate moieties; and (i.iii) from 1 to 49 wt% structural units derived from one or more types of monomers selected from ether bond-containing monomers represented by formulas (I) and (II): formula (I): wherein in formula (I), R_0 represents a hydrogen atom or CH_3 group, R represents a CH_2 group, CH_2CH_2 group or single bond, X represents a number 0-5 provided X represents a number 1-5 when R is a single bond, and R_1 is a hydrogen atom or C_1 to C_{20} organic group; formula (II). Wherein in formula (II), R_0 represents a hydrogen atom or CH_3 group, R represents a CH_2 group, CH_2CH_2 group or single bond, X represents a number 0-5, and R_1 is a hydrogen atom or C_1 to C_{20} organic group; and (ii) from 10wt % to 30wt% salt, wherein the salt is selected from sulphate salt and/or carbonate salt; and (b) from 0.1wt% to 5wt% hueing agent particle comprising: (i) from 2wt% to 10wt% hueing agent, wherein the hueing agent has the following structure: wherein the index values x and y are independently selected from 1 to 10; and (ii) from 60wt% to 98wt% clay.



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SOLID FREE-FLOWING PARTICULATE LAUNDRY DETERGENT COMPOSITION**FIELD OF THE INVENTION**

The present invention relates to solid free-flowing particulate laundry detergent compositions. The compositions of the present invention comprise a polymer particle and a hueing agent particle. The compositions of the present invention exhibit excellent cleaning and hueing performance, and also provide an improved deposition of hueing agent onto the fabric surface during laundering.

BACKGROUND OF THE INVENTION

Laundry detergent powder manufacturers seek to provide products that have excellent whiteness and cleaning performance. In order to meet this need, laundry detergent powder manufacturers incorporate ingredients such as hueing agents and polymers into their products. There are many different types of hueing agents and polymers available to the laundry detergent manufacturer and there are a variety of different methods these ingredients can be incorporated into a laundry detergent powder product. Particular care needs to be taken when incorporating hueing agents into a laundry detergent powder product to ensure that good hueing performance is achieved.

The inventors have found that the resultant whiteness and cleaning performance of the laundry detergent powder depends not only on the combination of the type of hueing agent and the type of polymer incorporated, but also on the particle architecture of the hueing agent particle and the polymer particle.

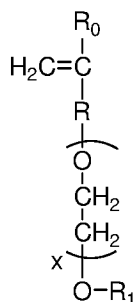
The inventors have found that when this particle architecture is optimized as defined by the claims of the present invention, the whiteness and cleaning performance of the laundry detergent powder product is improved. In addition, the inventors have found that this specific particle architecture also improves the deposition of the hueing agent onto the fabric surface during laundering.

SUMMARY OF THE INVENTION

The present invention relates to a solid free-flowing particulate laundry detergent composition comprising: (a) from 0.1wt% to 5wt% polymer particle comprising: (i) from 70wt% to 90wt% co-polymer, wherein the co-polymer comprises: (i.i) from 50 to less than 98 wt% structural units derived from one or more monomers comprising carboxyl groups; (i.ii) from 1 to less than 49 wt% structural units derived from one or more monomers comprising sulfonate

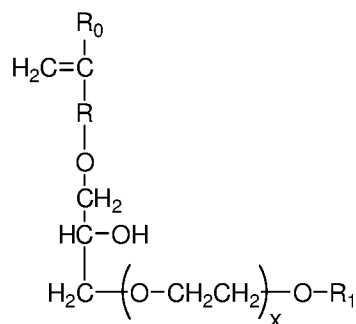
moieties; and (i.iii) from 1 to 49 wt% structural units derived from one or more types of monomers selected from ether bond-containing monomers represented by formulas (I) and (II):

formula (I):



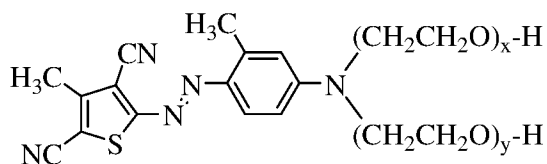
wherein in formula (I), R₀ represents a hydrogen atom or CH₃ group, R represents a CH₂ group, CH₂CH₂ group or single bond, X represents a number 0-5 provided X represents a number 1-5 when R is a single bond, and R₁ is a hydrogen atom or C₁ to C₂₀ organic group;

formula (II)



wherein in formula (II), R₀ represents a hydrogen atom or CH₃ group, R represents a CH₂ group, CH₂CH₂ group or single bond, X represents a number 0-5, and R₁ is a hydrogen atom or C₁ to C₂₀ organic group; and (ii) from 10wt% to 30wt% salt, wherein the salt is selected from sulphate salt and/or carbonate salt; and (b) from 0.1wt% to 5wt% hueing agent particle comprising: (i) from 2wt% to 10wt% hueing agent, wherein the hueing agent has the following structure:

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wherein the index values x and y are independently selected from 1 to 10; and (ii) from 60wt% to 98wt% clay.

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DETAILED DESCRIPTION OF THE INVENTION

Solid free-flowing particulate laundry detergent composition: The solid free-flowing particulate laundry detergent composition comprises from 0.1wt% to 5wt%, preferably from 0.5wt% to 2wt% polymer particle, and from 0.5wt% to 5wt%, preferably from 0.1wt% to 2wt% hueing agent particle. The polymer particle and hueing agent particle are described in more detail below. The composition preferably comprises from 35wt% to 80wt% spray-dried particle. The spray-dried particle is described in more detail below. The composition may also comprise: from 1wt% to 30wt% LAS particle; from 0.5wt% to 20wt%, preferably from 1wt% to 10wt% or even from 2wt% to 5wt% AES particle; and/or from 0.1wt% to 5wt%, preferably from 0.2wt% to 2wt% silicone particle. These particles are described in more detail below.

Preferably, the composition comprises: (a) from 0wt% to 5wt% zeolite builder; (b) from 0wt% to 5wt% phosphate builder; and (c) from 0wt% to 5wt% sodium carbonate.

Preferably, the composition comprises alkyl benzene sulphonate and ethoxylated alkyl sulphate in a weight ratio of from 5:1 to 20:1.

Typically, the solid free-flowing particulate laundry detergent composition is a fully formulated laundry detergent composition, not a portion thereof such as a spray-dried, extruded or agglomerate particle that only forms part of the laundry detergent composition. Typically, the solid composition comprises a plurality of chemically different particles, such as spray-dried base detergent particles and/or agglomerated base detergent particles and/or extruded base detergent particles, in combination with one or more, typically two or more, or five or more, or even ten or more particles selected from: surfactant particles, including surfactant agglomerates, surfactant extrudates, surfactant needles, surfactant noodles, surfactant flakes; phosphate particles; zeolite particles; silicate salt particles, especially sodium silicate particles; carbonate salt particles, especially sodium carbonate particles; polymer particles such as carboxylate polymer particles, cellulosic polymer particles, starch particles, polyester particles, polyamine particles, terephthalate polymer particles, polyethylene glycol particles; aesthetic particles such as coloured

noodles, needles, lamellae particles and ring particles; enzyme particles such as protease granulates, amylase granulates, lipase granulates, cellulase granulates, mannanase granulates, pectate lyase granulates, xyloglucanase granulates, bleaching enzyme granulates and co-granulates of any of these enzymes, preferably these enzyme granulates comprise sodium sulphate; bleach particles, such as percarbonate particles, especially coated percarbonate particles, such as percarbonate coated with carbonate salt, sulphate salt, silicate salt, borosilicate salt, or any combination thereof, perborate particles, bleach activator particles such as tetra acetyl ethylene diamine particles and/or alkyl oxybenzene sulphonate particles, bleach catalyst particles such as transition metal catalyst particles, and/or isoquinolinium bleach catalyst particles, pre-formed peracid particles, especially coated pre-formed peracid particles; filler particles such as sulphate salt particles and chloride particles; clay particles such as montmorillonite particles and particles of clay and silicone; flocculant particles such as polyethylene oxide particles; wax particles such as wax agglomerates; silicone particles, brightener particles; dye transfer inhibition particles; dye fixative particles; perfume particles such as perfume microcapsules and starch encapsulated perfume accord particles, or pro-perfume particles such as Schiff base reaction product particles; hueing dye particles; chelant particles such as chelant agglomerates; and any combination thereof.

Spray-dried particle: The spray-dried particle comprises: (a) from 8wt% to 24wt% alkyl benzene sulphonate anionic detergent surfactant; (b) from 5wt% to 18wt% silicate salt; (c) from 0wt% to 10wt% sodium carbonate; and (d) from 0wt% to 5wt% carboxylate polymer.

Preferably, the spray-dried particle is free from sodium carbonate. Preferably, the spray-dried particle comprises sulphate salt, preferably sodium sulphate. Preferably, the spray-dried particle comprises from 54wt% to 87wt% sodium sulphate.

Preferably, the spray-dried particle comprises from 5wt% to 18wt% silicate salt, wherein the ratio of SiO_2 : Na_2O is in the range of from 1.6 to 2.35. It may be preferred that when the silicate salt has a low SiO_2 : Na_2O ratio, for example approximately 1.6, then the level of silicate salt present in the spray-dried particle is high, for example approximately 18wt%. It may also be preferred than when the silicate has a high SiO_2 : Na_2O ratio, for example approximately 2.35, then the level of silicate salt present in the spray-dried particle is low, for example approximately 5wt%.

Preferably, the spray-dried particle has a bulk density of from 350g/l to 500g/l. Typically, the spray-dried particle has a weight average particle size of from 400 micrometers to 450 micrometers. Typically, the spray-dried particle has a particle size distribution such that the geometric span is from 1.8 to 2.0.

Method of making the spray-dried particle: The spray-dried particle is prepared by a spray-drying process. Typically, an aqueous mixture is prepared by contacting alkyl benzene sulphonate anionic deterative surfactant, silicate salt and water. If present, carboxylate polymer is then added to the aqueous mixture. Typically, sodium sulphate is then contacted to the aqueous mixture to form a crutcher mixture. Typically, the crutcher mixture comprises from 26wt% to 32wt% water. Typically, the crutcher mixture is then spray-dried to form the spray-dried particle.

LAS particle: The LAS particle comprises: (a) from 30wt% to 50wt% alkyl benzene sulphonate anionic deterative surfactant; and (b) from 50wt% to 70wt% salt, wherein the salt is a sodium salt and/or a carbonate salt. Preferably, the LAS particle comprises from 1wt% to 5wt% carboxylate polymer. The LAS particle can be an LAS agglomerate or an LAS spray-dried particle. Typically, the LAS spray-dried particle has a bulk density of from 300g/l to 400g/l.

Method of making the LAS particle: The LAS particle is preferably prepared by either an agglomeration process or a spray-drying process.

Typically, the spray-drying process comprises the step of contacting alkyl benzene sulphonate anionic deterative surfactant and water to form an aqueous mixture. Preferably, if present the carboxylate polymer is then contacted with the aqueous mixture. Typically, salt is then contacted with the aqueous mixture to form a crutcher mixture. Typically, the crutcher mixture comprises at least 40wt% water. This level of water in the crutcher is preferred, especially when the salt is sodium sulphate. This is because this level of water promotes good dissolution of the sodium sulphate in the crutcher mixture. Typically, the crutcher mixture is then spray-dried to form the LAS spray-dried particle.

Preferably, the inlet air temperature during the spray-drying step is 250°C or lower. Controlling the inlet air temperature of the spray-drying step in this manner is important due to the thermal stability of the crutcher mixture due to the high organic level in the crutcher mixture.

The spray-drying step can be co-current or counter-current.

AES particle: The AES particle comprises: (a) from 40wt% to 60wt% partially ethoxylated alkyl sulphate anionic deterative surfactant, wherein the partially ethoxylated alkyl sulphate anionic deterative surfactant has a molar average degree of ethoxylation of from 0.8 to 1.2, and wherein the partially ethoxylated alkyl sulphate anionic deterative surfactant has a molar ethoxylation distribution such that: (i) from 40wt% to 50wt% is unethoxylated, having a degree of ethoxylation of 0; (ii) from 20wt% to 30wt% has a degree of ethoxylation of 1; (iii) from 20wt% to 40wt% has a degree of ethoxylation of 2 or greater; (b) from 20wt% to 50wt% salt, wherein the salt is selected from sulphate salt and/or carbonate salt; and (c) from 10wt% to 30wt% silica. Preferably, the weight ratio of partially ethoxylated alkyl sulphate anionic deterative

surfactant to silica is from 1.3:1 to 6:1, preferably from 2:1 to 5:1. Preferably, the AES particle is in the form of an agglomerate.

Method of making partially ethoxylated alkyl sulphate anionic deterative surfactant:

Ethylene oxide and alkyl alcohol are reacted together to form ethoxylated alkyl alcohol, typically the molar ratio of ethylene oxide to alkyl alcohol used as the reaction substrates is in the range of from 0.8 to 1.2, preferably a stoichiometric ratio is used (a molar ratio of 1:1). Typically, a catalyst and alkyl alcohol are mixed together and dried using vacuum and heat (e.g. 100 mbar and 140°C) to form an alcohol-catalyst. Typically, ethylene oxide (EO) is then slowly added to the dried alcohol-catalyst. Typically, after the EO is added dried alcohol-catalyst, the pH of the reaction mixture is reduced, e.g. by using lactic acid. Typically, acetic acid is then added to neutralize the reaction to form the ethoxylated alkyl alcohol.

Typically, the ethoxylated alkyl alcohol is sulphated in a falling film reactor with SO_3 to form a surfactant acid precursor, which is then neutralized with NaOH to form the ethoxylated alkyl sulphate anionic deterative surfactant (AES).

Typically, the molar ethoxylation distribution of AES is manipulated by controlling the molar ethoxylation distribution of the ethoxylated alcohol product during its synthesis. The catalyst for this reaction is preferably a base with a $\text{pK}_b \leq 5$, more preferably with a $\text{pK}_b \leq 3$, more preferably with a $\text{pK}_b \leq 1$, most preferably with a $\text{pK}_b \leq 0.5$. Preferred catalysts are KOH and NaOH. Typically, the choice of catalyst controls the molar ethoxylation distribution. Typically, stronger base catalysts will favor a broader molar ethoxylation distribution with higher levels of unethoxylated material and higher levels of ethoxylated materials having a degree of ethoxylation of 2 or greater. Typically, weaker base catalysts favor a narrower molar ethoxylation distribution with lower levels of unethoxylated alcohol and lower levels of ethoxylated material having a degree of ethoxylation of 2 or greater.

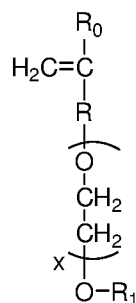
The molar ethoxylation distribution of the AES is typically determined by measuring the molecular weight distribution via mass spectrometry.

Method of making the AES particle: Typically, AES particle is made by an agglomeration process. Typically, the partially ethoxylated alkyl sulphate anionic deterative surfactant, salt and silica are dosed into one or more mixers and agglomerated to form the AES particle.

Polymer particle: Typically, the polymer particle comprises: (a) from 60wt% to 90wt% co-polymer and (b) from 10wt% to 40wt% salt. Preferably, the co-polymer comprises: (i) from 50 to less than 98 wt% structural units derived from one or more monomers comprising carboxyl groups; (ii) from 1 to less than 49 wt% structural units derived from one or more monomers

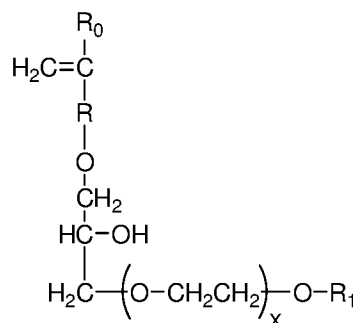
comprising sulfonate moieties; and (iii) from 1 to 49 wt% structural units derived from one or more types of monomers selected from ether bond-containing monomers represented by formulas (I) and (II):

5 formula (I):



wherein in formula (I), R_0 represents a hydrogen atom or CH_3 group, R represents a CH_2 group, CH_2CH_2 group or single bond, X represents a number 0-5 provided X represents a number 1-5
 10 when R is a single bond, and R_1 is a hydrogen atom or C_1 to C_{20} organic group;

formula (II)



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wherein in formula (II), R_0 represents a hydrogen atom or CH_3 group, R represents a CH_2 group, CH_2CH_2 group or single bond, X represents a number 0-5, and R_1 is a hydrogen atom or C_1 to C_{20} organic group.

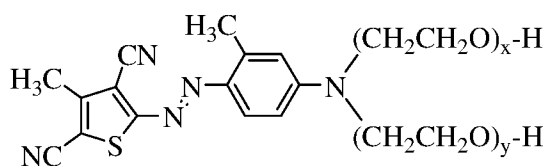
It may be preferred that the polymer has a weight average molecular weight of at least
 20 50kDa, or even at least 70kDa.

Preferably, the salt is selected from sulphate salt and/or carbonate salt. A preferred salt is a sulphate salt, more preferably sodium sulphate. Preferably, the polymer particle is a spray-dried particle. Typically, the polymer particle has a bulk density of from 300g/l to 500g/l. Typically,

the polymer particle has a weight average particle size in the range of from 300 micrometers to 500 micrometers. Typically, the particle size distribution of the polymer particle is such that the geometric span is from 1.8 to 2.0.

Method of making the polymer particle: Typically, the polymer particle is prepared by a spray-drying process. Preferably, the polymer is contacted to water to form an aqueous polymer mixture. Preferably, salt is then contacted to this aqueous polymer mixture to form a crutcher mixture. Preferably, the crutcher mixture comprises from 60wt% to 80wt% water. Preferably, the crutcher mixture is then spray dried to form the polymer particle. This order of addition ensures good dispersion of the polymer in the crutcher mixture, which in turn leads to good drying profile and good physical properties of the polymer particle, such as good cake strength profile.

Hueing agent particle: The particle comprises: (a) from 2wt% to 10wt% hueing agent, wherein the hueing agent has the following structure:



wherein the index values x and y are independently selected from 1 to 10; and (b) from 60wt% to 98wt% clay. Preferably, the clay is a montmorillonite clay, also known as bentonite clay. The particle may also comprise an inorganic salt, preferably from 10wt% to 30wt% inorganic salt. A preferred inorganic salt is sodium sulphate, although other inorganic salts such as sodium carbonate and/or sodium bicarbonate may also be used. Preferably the particle comprises from 10wt% to 30wt% sodium sulphate.

In some aspects, the hueing agent has an average degree of ethoxylation, $x + y$, sometimes also referred to as the average number of ethoxylate groups, of from about 3 to about 12, preferably from about 4 to about 8. In some embodiments the average degree of ethoxylation, $x + y$, can be from about 5 to about 6. The range of ethoxylation present in the mixture varies depending on the average number of ethoxylates incorporated. The hueing agent is synthesized according to the procedures disclosed in US4912203 to Kluger et al.; a primary aromatic amine is reacted with an appropriate amount of ethylene oxide, according to procedures well known in the art. The polyethyleneoxy substituted m-toluidine useful in the preparation of the colorant can be prepared by a number of well known methods. It is preferred, however, that the polyethyleneoxy groups be introduced into the m-toluidine molecule by reaction of the m-toluidine with ethylene

oxide. Generally the reaction proceeds in two steps, the first being the formation of the corresponding N,N-dihydroxyethyl substituted m-toluidine. In some aspects, no catalyst is utilized in this first step (for example as disclosed at Column 4, lines 16-25 of US3927044 to Foster et al.). The dihydroxyethyl substituted m-toluidine is then reacted with additional ethylene oxide in the presence of a catalyst such as sodium (described in Preparation II of US3157633 to Kuhn), or it may be reacted with additional ethylene oxide in the presence of sodium or potassium hydroxide (described in Example 5 of US5071440 to Hines et al.). The amount of ethylene oxide added to the reaction mixture determines the number of ethyleneoxy groups which ultimately attach to the nitrogen atom. In some aspects, an excess of the polyethyleneoxy substituted m-toluidine coupler may be employed in the formation of the whitening agent and remain as a component in the final colorant mixture. In certain aspects, the presence of excess coupler may confer advantageous properties to a mixture in which it is incorporated such as the raw material, a pre-mix, a finished product or even the wash solution prepared from the finished product.

Method of making the hueing agent particle: The hueing agent particle can be prepared by an agglomeration process. Typically, the hueing agent and clay are dosed into one or more mixers and agglomerated to form the hueing agent agglomerate.

Silicone particle: The silicone particle comprises: (a) from 10wt% to 20wt% silicone; and (b) from 50wt% to 80wt% carrier. The carrier may be zeolite. The silicone particle may be in the form of an agglomerate.

Method of making the silicone particle: The silicone particle can be prepared by an agglomeration process. Typically, the silicone and carrier are dosed into one or more mixers and agglomerated to form the silicone agglomerate.

Detergent ingredients: Typically, suitable laundry detergent compositions comprise a detergent ingredient selected from: deterative surfactant, such as anionic deterative surfactants, non-ionic deterative surfactants, cationic deterative surfactants, zwitterionic deterative surfactants and amphoteric deterative surfactants; polymers, such as carboxylate polymers, soil release polymer, anti-redeposition polymers, cellulosic polymers and care polymers; bleach, such as sources of hydrogen peroxide, bleach activators, bleach catalysts and pre-formed peracids; photobleach, such as such as zinc and/or aluminium sulphonated phthalocyanine; enzymes, such as proteases, amylases, cellulases, lipases; zeolite builder; phosphate builder; co-builders, such as citric acid and citrate; carbonate, such as sodium carbonate and sodium bicarbonate; sulphate salt, such as sodium sulphate; silicate salt such as sodium silicate; chloride salt, such as sodium chloride; brighteners; chelants; hueing agents; dye transfer inhibitors; dye fixative agents;

perfume; silicone; fabric softening agents, such as clay; flocculants, such as polyethyleneoxide; suds suppressors; and any combination thereof.

Detergent surfactant: Suitable detergent surfactants include anionic detergent surfactants, non-ionic detergent surfactant, cationic detergent surfactants, zwitterionic detergent surfactants and amphoteric detergent surfactants. Suitable detergent surfactants may be linear or branched, substituted or un-substituted, and may be derived from petrochemical material or biomaterial.

Anionic detergent surfactant: Suitable anionic detergent surfactants include sulphonate and sulphate detergent surfactants.

5 Suitable sulphonate detergent surfactants include methyl ester sulphonates, alpha olefin sulphonates, alkyl benzene sulphonates, especially alkyl benzene sulphonates, 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, other suitable LAB include high 2-phenyl LAB, such as those
10 supplied by Sasol under the tradename Hyblene®.

 Suitable sulphate detergent surfactants include alkyl sulphate, preferably C₈₋₁₈ alkyl sulphate, or predominantly C₁₂ alkyl sulphate.

 A preferred sulphate detergent surfactant is alkyl alkoxyated sulphate, preferably alkyl ethoxyated sulphate, preferably a C₈₋₁₈ alkyl alkoxyated sulphate, preferably a C₈₋₁₈ alkyl
15 ethoxyated 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 ethoxyated sulphate having an average degree of ethoxylation of from 0.5 to 10, preferably from 0.5 to 5, more preferably from 0.5 to 3 and most preferably from 0.5 to 1.5.

20 The alkyl sulphate, alkyl alkoxyated sulphate and alkyl benzene sulphonates may be linear or branched, substituted or un-substituted, and may be derived from petrochemical material or biomaterial.

 Other suitable anionic detergent surfactants include alkyl ether carboxylates.

 Suitable anionic detergent surfactants may be in salt form, suitable counter-ions include
25 sodium, calcium, magnesium, amino alcohols, and any combination thereof. A preferred counter-ion is sodium.

Non-ionic detergent surfactant: Suitable non-ionic detergent surfactants are selected from the group consisting of: C₈-C₁₈ alkyl ethoxylates, such as, NEODOL® non-ionic surfactants from Shell; C₆-C₁₂ alkyl phenol alkoxyates wherein preferably 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; alkylpolysaccharides, preferably alkylpolyglycosides; methyl ester ethoxylates; polyhydroxy fatty acid amides; ether capped poly(oxyalkylated) alcohol surfactants; and mixtures thereof.

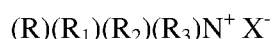
Suitable non-ionic deterative surfactants are alkylpolyglucoside and/or an alkyl alkoxyated alcohol.

Suitable non-ionic deterative surfactants include alkyl alkoxyated alcohols, preferably 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 nonionic deterative surfactants include secondary alcohol-based deterative surfactants.

Cationic deterative surfactant: Suitable cationic deterative surfactants include alkyl pyridinium compounds, alkyl quaternary ammonium compounds, alkyl quaternary phosphonium compounds, alkyl ternary sulphonium compounds, and mixtures thereof.

Preferred cationic deterative 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.

Zwitterionic deterative surfactant: Suitable zwitterionic deterative surfactants include amine oxides and/or betaines.

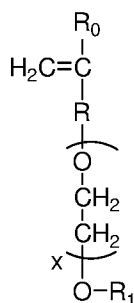
Polymer: Suitable polymers include carboxylate polymers, soil release polymers, anti-redeposition polymers, cellulosic polymers, care polymers and any combination thereof.

Carboxylate polymer: The composition may comprise a carboxylate polymer, such as a maleate/acrylate random copolymer or polyacrylate homopolymer. Suitable carboxylate polymers include: polyacrylate homopolymers having a molecular weight of from 4,000 Da to

9,000 Da; maleate/acrylate random copolymers having a molecular weight of from 50,000 Da to 100,000 Da, or from 60,000 Da to 80,000 Da.

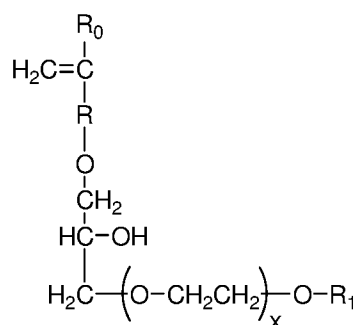
Another suitable carboxylate polymer is a co-polymer that comprises: (i) from 50 to less than 98 wt% structural units derived from one or more monomers comprising carboxyl groups;
 5 (ii) from 1 to less than 49 wt% structural units derived from one or more monomers comprising sulfonate moieties; and (iii) from 1 to 49 wt% structural units derived from one or more types of monomers selected from ether bond-containing monomers represented by formulas (I) and (II):

formula (I):



wherein in formula (I), R_0 represents a hydrogen atom or CH_3 group, R represents a CH_2 group, CH_2CH_2 group or single bond, X represents a number 0-5 provided X represents a number 1-5 when R is a single bond, and R_1 is a hydrogen atom or C_1 to C_{20} organic group;

formula (II)



wherein in formula (II), R_0 represents a hydrogen atom or CH_3 group, R represents a CH_2 group, CH_2CH_2 group or single bond, X represents a number 0-5, and R_1 is a hydrogen atom or C_1 to C_{20} organic group.

It may be preferred that the polymer has a weight average molecular weight of at least 50kDa, or even at least 70kDa.

Soil release polymer: The composition may comprise a soil release polymer. A suitable soil release polymer has a structure as defined by one of the following structures (I), (II) or (III):



wherein:

a, b and c are from 1 to 200;

d, e and f are from 1 to 50;

15 Ar is a 1,4-substituted phenylene;

sAr is 1,3-substituted phenylene substituted in position 5 with SO₃Me;

Me is Li, K, Mg/2, Ca/2, Al/3, ammonium, mono-, di-, tri-, or tetraalkylammonium wherein the alkyl groups are C₁-C₁₈ alkyl or C₂-C₁₀ hydroxyalkyl, or mixtures thereof;

R¹, R², R³, R⁴, R⁵ and R⁶ are independently selected from H or C₁-C₁₈ n- or iso-alkyl; and

20 R⁷ is a linear or branched C₁-C₁₈ alkyl, or a linear or branched C₂-C₃₀ alkenyl, or a cycloalkyl group with 5 to 9 carbon atoms, or a C₈-C₃₀ aryl group, or a C₆-C₃₀ arylalkyl group.

Suitable soil release polymers are sold by Clariant under the TexCare® series of polymers, e.g.

TexCare® SRN240 and TexCare® SRA300. Other suitable soil release polymers are sold by

Solvay under the Repel-o-Tex® series of polymers, e.g. Repel-o-Tex® SF2 and Repel-o-Tex®

25 Crystal.

Anti-redeposition polymer: Suitable anti-redeposition polymers include polyethylene glycol polymers and/or polyethyleneimine polymers.

Suitable polyethylene glycol polymers include random graft co-polymers comprising: (i) hydrophilic backbone comprising polyethylene glycol; and (ii) hydrophobic side chain(s)

30 selected from the group consisting of: C₄-C₂₅ alkyl group, polypropylene, polybutylene, vinyl ester of a saturated C₁-C₆ mono-carboxylic acid, C₁-C₆ alkyl ester of acrylic or methacrylic acid, and mixtures thereof. Suitable polyethylene glycol polymers have a polyethylene glycol backbone with random grafted polyvinyl acetate side chains. The average molecular weight of the polyethylene glycol backbone can be in the range of from 2,000 Da to 20,000 Da, or from

4,000 Da to 8,000 Da. The molecular weight ratio of the polyethylene glycol backbone to the polyvinyl acetate side chains can be in the range of from 1:1 to 1:5, or from 1:1.2 to 1:2. The average number of graft sites per ethylene oxide units can be less than 1, or less than 0.8, the average number of graft sites per ethylene oxide units can be in the range of from 0.5 to 0.9, or the average number of graft sites per ethylene oxide units can be in the range of from 0.1 to 0.5, or from 0.2 to 0.4. A suitable polyethylene glycol polymer is Sokalan HP22. Suitable polyethylene glycol polymers are described in WO08/007320.

Cellulosic polymer: Suitable cellulosic polymers are selected from alkyl cellulose, alkyl alkoxyalkyl cellulose, carboxyalkyl cellulose, alkyl carboxyalkyl cellulose, sulphaalkyl cellulose, more preferably selected from carboxymethyl cellulose, methyl cellulose, methyl hydroxyethyl cellulose, methyl carboxymethyl cellulose, and mixtures thereof.

Suitable carboxymethyl celluloses have a degree of carboxymethyl substitution from 0.5 to 0.9 and a molecular weight from 100,000 Da to 300,000 Da.

Suitable carboxymethyl celluloses have a degree of substitution greater than 0.65 and a degree of blockiness greater than 0.45, e.g. as described in WO09/154933.

Care polymers: Suitable care polymers include cellulosic polymers that are cationically modified or hydrophobically modified. Such modified cellulosic polymers can provide anti-abrasion benefits and dye lock benefits to fabric during the laundering cycle. Suitable cellulosic polymers include cationically modified hydroxyethyl cellulose.

Other suitable care polymers include dye lock polymers, for example the condensation oligomer produced by the condensation of imidazole and epichlorhydrin, preferably in ratio of 1:4:1. A suitable commercially available dye lock polymer is Polyquart® FDI (Cognis).

Other suitable care polymers include amino-silicone, which can provide fabric feel benefits and fabric shape retention benefits.

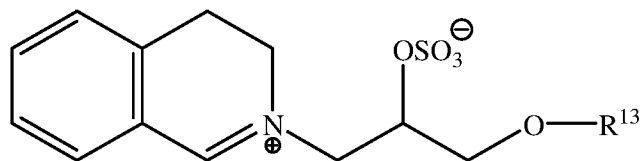
Bleach: Suitable bleach includes sources of hydrogen peroxide, bleach activators, bleach catalysts, pre-formed peracids and any combination thereof. A particularly suitable bleach includes a combination of a source of hydrogen peroxide with a bleach activator and/or a bleach catalyst.

Source of hydrogen peroxide: Suitable sources of hydrogen peroxide include sodium perborate and/or sodium percarbonate.

Bleach activator: Suitable bleach activators include tetra acetyl ethylene diamine and/or alkyl oxybenzene sulphonate.

Bleach catalyst: The composition may comprise a bleach catalyst. Suitable bleach catalysts include oxaziridinium bleach catalysts, transition metal bleach catalysts, especially

manganese and iron bleach catalysts. A suitable bleach catalyst has a structure corresponding to general formula below:



wherein R^{13} is selected from the group consisting of 2-ethylhexyl, 2-propylheptyl, 2-butyloctyl, 2-pentylononyl, 2-hexyldecyl, n-dodecyl, n-tetradecyl, n-hexadecyl, n-octadecyl, iso-nonyl, iso-decyl, iso-tridecyl and iso-pentadecyl.

Pre-formed peracid: Suitable pre-form peracids include phthalimido-peroxycaproic acid.

Enzymes: Suitable enzymes include lipases, proteases, cellulases, amylases and any combination thereof.

Protease: Suitable proteases include metalloproteases and/or serine proteases. Examples of suitable neutral or alkaline proteases include: subtilisins (EC 3.4.21.62); trypsin-type or chymotrypsin-type proteases; and metalloproteases. The suitable proteases include chemically or genetically modified mutants of the aforementioned suitable proteases.

Suitable commercially available protease enzymes include those sold under the trade names Alcalase®, Savinase®, Primase®, Durazym®, Polarzyme®, Kannase®, Liquease®, Liquease Ultra®, Savinase Ultra®, Ovozime®, Neutrase®, Everlase® and Esperase® by Novozymes A/S (Denmark), those sold under the tradename Maxatase®, Maxacal®, Maxapem®, Preferenz P® series of proteases including Preferenz® P280, Preferenz® P281, Preferenz® P2018-C, Preferenz® P2081-WE, Preferenz® P2082-EE and Preferenz® P2083-A/J, Properase®, Purafect®, Purafect Prime®, Purafect Ox®, FN3®, FN4®, Excellase® and Purafect OXP® by DuPont, those sold under the tradename Opticlean® and Optimase® by Solvay Enzymes, those available from Henkel/ Kemira, namely BLAP (sequence shown in Figure 29 of US 5,352,604 with the following mutations S99D + S101 R + S103A + V104I + G159S, hereinafter referred to as BLAP), BLAP R (BLAP with S3T + V4I + V199M + V205I + L217D), BLAP X (BLAP with S3T + V4I + V205I) and BLAP F49 (BLAP with S3T + V4I + A194P + V199M + V205I + L217D) - all from Henkel/Kemira; and KAP (Bacillus alkalophilus subtilisin with mutations A230V + S256G + S259N) from Kao.

A suitable protease is described in WO11/140316 and WO11/072117.

Amylase: Suitable amylases are derived from AA560 alpha amylase endogenous to Bacillus sp. DSM 12649, preferably having the following mutations: R118K, D183*, G184*,

N195F, R320K, and/or R458K. Suitable commercially available amylases include Stainzyme®, Stainzyme® Plus, Natalase, Termamyl®, Termamyl® Ultra, Liquezyme® SZ, Duramyl®, Everest® (all Novozymes) and Spezyme® AA, Preferenz S® series of amylases, Purastar® and Purastar® Ox Am, Optimize® HT Plus (all Du Pont).

5 A suitable amylase is described in WO06/002643.

Cellulase: Suitable cellulases include those of bacterial or fungal origin. Chemically modified or protein engineered mutants are also suitable. Suitable cellulases include cellulases from the genera *Bacillus*, *Pseudomonas*, *Humicola*, *Fusarium*, *Thielavia*, *Acremonium*, e.g., the fungal cellulases produced from *Humicola insolens*, *Myceliophthora thermophila* and *Fusarium*
10 *oxysporum*.

Commercially available cellulases include Celluzyme®, Carezyme®, and Carezyme® Premium, Celluclean® and Whitezyme® (Novozymes A/S), Revitalenz® series of enzymes (Du Pont), and Biotouch® series of enzymes (AB Enzymes). Suitable commercially available cellulases include Carezyme® Premium, Celluclean® Classic. Suitable cellulases are described
15 in WO07/144857 and WO10/056652.

Lipase: Suitable lipases include those of bacterial, fungal or synthetic origin, and variants thereof. Chemically modified or protein engineered mutants are also suitable. Examples of suitable lipases include lipases from *Humicola* (synonym *Thermomyces*), e.g., from *H. lanuginosa* (*T. lanuginosus*).

20 The lipase may be a “first cycle lipase”, e.g. such as those described in WO06/090335 and WO13/116261. In one aspect, the lipase is a first-wash lipase, preferably a variant of the wild-type lipase from *Thermomyces lanuginosus* comprising T231R and/or N233R mutations. Preferred lipases include those sold under the tradenames Lipex®, Lipolex® and Lipoclean® by Novozymes, Bagsvaerd, Denmark.

25 Other suitable lipases include: Liprl 139, e.g. as described in WO2013/171241; and TfuLip2, e.g. as described in WO2011/084412 and WO2013/033318.

Other enzymes: Other suitable enzymes are bleaching enzymes, such as peroxidases/oxidases, which include those of plant, bacterial or fungal origin and variants thereof. Commercially available peroxidases include Guardzyme® (Novozymes A/S). Other
30 suitable enzymes include choline oxidases and perhydrolases such as those used in Gentle Power Bleach™.

Other suitable enzymes include pectate lyases sold under the tradenames X-Pect®, Pectaway® (from Novozymes A/S, Bagsvaerd, Denmark) and PrimaGreen® (DuPont) and

mannanases sold under the tradenames Mannaway® (Novozymes A/S, Bagsvaerd, Denmark), and Mannastar® (Du Pont).

Zeolite builder: The composition may comprise zeolite builder. The composition may comprise from 0wt% to 5wt% zeolite builder, or 3wt% zeolite builder. The composition may even be substantially free of zeolite builder; substantially free means “no deliberately added”. Typical zeolite builders include zeolite A, zeolite P and zeolite MAP.

Phosphate builder: The composition may comprise phosphate builder. The composition may comprise from 0wt% to 5wt% phosphate builder, or to 3wt%, phosphate builder. The composition may even be substantially free of phosphate builder; substantially free means “no deliberately added”. A typical phosphate builder is sodium tri-polyphosphate.

Carbonate salt: The composition may comprise carbonate salt. The composition may comprise from 0wt% to 10wt% carbonate salt, or to 5wt% carbonate salt. The composition may even be substantially free of carbonate salt; substantially free means “no deliberately added”. Suitable carbonate salts include sodium carbonate and sodium bicarbonate.

Silicate salt: The composition may comprise silicate salt. The composition may comprise from 0wt% to 10wt% silicate salt, or to 5wt% silicate salt. A preferred silicate salt is sodium silicate, especially preferred are sodium silicates having a $\text{Na}_2\text{O}:\text{SiO}_2$ ratio of from 1.0 to 2.8, preferably from 1.6 to 2.0.

Sulphate salt: A suitable sulphate salt is sodium sulphate.

Brightener: Suitable fluorescent brighteners include: di-styryl biphenyl compounds, e.g. Tinopal® CBS-X, di-amino stilbene di-sulfonic acid compounds, e.g. Tinopal® DMS pure Xtra and Blankophor® HRH, and Pyrazoline compounds, e.g. Blankophor® SN, and coumarin compounds, e.g. Tinopal® SWN.

Preferred brighteners are: sodium 2 (4-styryl-3-sulfophenyl)-2H-naphthol[1,2-d]triazole, disodium 4,4'-bis{[(4-anilino-6-(N methyl-N-2 hydroxyethyl)amino 1,3,5-triazin-2-yl)];amino} stilbene-2,2'-disulfonate, disodium 4,4'-bis{[(4-anilino-6-morpholino-1,3,5-triazin-2-yl)]amino} stilbene-2,2'-disulfonate, and disodium 4,4'-bis(2-sulfostyryl)biphenyl. A suitable fluorescent brightener is C.I. Fluorescent Brightener 260, which may be used in its beta or alpha crystalline forms, or a mixture of these forms.

Chelant: The composition may also comprise a chelant selected from: diethylene triamine pentaacetate, diethylene triamine penta(methyl phosphonic acid), ethylene diamine-N'N'-disuccinic acid, ethylene diamine tetraacetate, ethylene diamine tetra(methylene phosphonic acid) and hydroxyethane di(methylene phosphonic acid). A preferred chelant is ethylene diamine-N'N'-disuccinic acid (EDDS) and/or hydroxyethane diphosphonic acid (HEDP). The

composition preferably comprises ethylene diamine-N'N'-disuccinic acid or salt thereof. Preferably the ethylene diamine-N'N'-disuccinic acid is in S,S enantiomeric form. Preferably the composition comprises 4,5-dihydroxy-m-benzenedisulfonic acid disodium salt. Preferred chelants may also function as calcium carbonate crystal growth inhibitors such as: 1-hydroxyethanediphosphonic acid (HEDP) and salt thereof; N,N-dicarboxymethyl-2-aminopentane-1,5-dioic acid and salt thereof; 2-phosphonobutane-1,2,4-tricarboxylic acid and salt thereof; and combination thereof.

Hueing agent: Suitable hueing agents include small molecule dyes, typically falling into the Colour Index (C.I.) classifications of Acid, Direct, Basic, Reactive (including hydrolysed forms thereof) or Solvent or Disperse dyes, for example classified as Blue, Violet, Red, Green or Black, and provide the desired shade either alone or in combination. Preferred such hueing agents include Acid Violet 50, Direct Violet 9, 66 and 99, Solvent Violet 13 and any combination thereof.

Many hueing agents are known and described in the art which may be suitable for the present invention, such as hueing agents described in WO2014/089386.

Suitable hueing agents include phthalocyanine and azo dye conjugates, such as described in WO2009/069077.

Suitable hueing agents may be alkoxyated. Such alkoxyated compounds may be produced by organic synthesis that may produce a mixture of molecules having different degrees of alkoxylation. Such mixtures may be used directly to provide the hueing agent, or may undergo a purification step to increase the proportion of the target molecule. Suitable hueing agents include alkoxyated bis-azo dyes, such as described in WO2012/054835, and/or alkoxyated thiophene azo dyes, such as described in WO2008/087497 and WO2012/166768.

The hueing agent may be incorporated into the detergent composition as part of a reaction mixture which is the result of the organic synthesis for a dye molecule, with optional purification step(s). Such reaction mixtures generally comprise the dye molecule itself and in addition may comprise un-reacted starting materials and/or by-products of the organic synthesis route. Suitable hueing agents can be incorporated into hueing dye particles, such as described in WO 2009/069077.

Dye transfer inhibitors: Suitable dye transfer inhibitors include polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidone, polyvinylloxazolidone, polyvinylimidazole and mixtures thereof. Preferred are poly(vinyl pyrrolidone), poly(vinylpyridine betaine), poly(vinylpyridine N-oxide), poly(vinyl pyrrolidone-vinyl imidazole) and mixtures thereof. Suitable commercially available dye transfer inhibitors

include PVP-K15 and K30 (Ashland), Sokalan® HP165, HP50, HP53, HP59, HP56K, HP56, HP66 (BASF), Chromabond® S-400, S403E and S-100 (Ashland).

Perfume: Suitable perfumes comprise perfume materials selected from the group: (a) perfume materials having a ClogP of less than 3.0 and a boiling point of less than 250°C (quadrant 1 perfume materials); (b) perfume materials having a ClogP of less than 3.0 and a boiling point of 250°C or greater (quadrant 2 perfume materials); (c) perfume materials having a ClogP of 3.0 or greater and a boiling point of less than 250°C (quadrant 3 perfume materials); (d) perfume materials having a ClogP of 3.0 or greater and a boiling point of 250°C or greater (quadrant 4 perfume materials); and (e) mixtures thereof.

It may be preferred for the perfume to be in the form of a perfume delivery technology. Such delivery technologies further stabilize and enhance the deposition and release of perfume materials from the laundered fabric. Such perfume delivery technologies can also be used to further increase the longevity of perfume release from the laundered fabric. Suitable perfume delivery technologies include: perfume microcapsules, pro-perfumes, polymer assisted deliveries, molecule assisted deliveries, fiber assisted deliveries, amine assisted deliveries, cyclodextrin, starch encapsulated accord, zeolite and other inorganic carriers, and any mixture thereof. A suitable perfume microcapsule is described in WO2009/101593.

Silicone: Suitable silicones include polydimethylsiloxane and amino-silicones. Suitable silicones are described in WO05075616.

Process for making the solid composition: Typically, the particles of the composition can be prepared by any suitable method. For example: spray-drying, agglomeration, extrusion and any combination thereof.

Typically, a suitable spray-drying process comprises the step of forming an aqueous slurry mixture, transferring it through at least one pump, preferably two pumps, to a pressure nozzle. Atomizing the aqueous slurry mixture into a spray-drying tower and drying the aqueous slurry mixture to form spray-dried particles. Preferably, the spray-drying tower is a counter-current spray-drying tower, although a co-current spray-drying tower may also be suitable.

Typically, the spray-dried powder is subjected to cooling, for example an air lift. Typically, the spray-drying powder is subjected to particle size classification, for example a sieve, to obtain the desired particle size distribution. Preferably, the spray-dried powder has a particle size distribution such that weight average particle size is in the range of from 300 micrometers to 500 micrometers, and less than 10wt% of the spray-dried particles have a particle size greater than 2360 micrometers.

It may be preferred to heat the aqueous slurry mixture to elevated temperatures prior to atomization into the spray-drying tower, such as described in WO2009/158162.

It may be preferred for anionic surfactant, such as linear alkyl benzene sulphonate, to be introduced into the spray-drying process after the step of forming the aqueous slurry mixture: for example, introducing an acid precursor to the aqueous slurry mixture after the pump, such as described in WO 09/158449.

It may be preferred for a gas, such as air, to be introduced into the spray-drying process after the step of forming the aqueous slurry, such as described in WO2013/181205.

It may be preferred for any inorganic ingredients, such as sodium sulphate and sodium carbonate, if present in the aqueous slurry mixture, to be micronized to a small particle size such as described in WO2012/134969.

Typically, a suitable agglomeration process comprises the step of contacting a detergent ingredient, such as a detergent surfactant, e.g. linear alkyl benzene sulphonate (LAS) and/or alkyl alkoxylated sulphate, with an inorganic material, such as sodium carbonate and/or silica, in a mixer. The agglomeration process may also be an in-situ neutralization agglomeration process wherein an acid precursor of a detergent surfactant, such as LAS, is contacted with an alkaline material, such as carbonate and/or sodium hydroxide, in a mixer, and wherein the acid precursor of a detergent surfactant is neutralized by the alkaline material to form a detergent surfactant during the agglomeration process.

Other suitable detergent ingredients that may be agglomerated include polymers, chelants, bleach activators, silicones and any combination thereof.

The agglomeration process may be a high, medium or low shear agglomeration process, wherein a high shear, medium shear or low shear mixer is used accordingly. The agglomeration process may be a multi-step agglomeration process wherein two or more mixers are used, such as a high shear mixer in combination with a medium or low shear mixer. The agglomeration process can be a continuous process or a batch process.

It may be preferred for the agglomerates to be subjected to a drying step, for example to a fluid bed drying step. It may also be preferred for the agglomerates to be subjected to a cooling step, for example a fluid bed cooling step.

Typically, the agglomerates are subjected to particle size classification, for example a fluid bed elutriation and/or a sieve, to obtain the desired particle size distribution. Preferably, the agglomerates have a particle size distribution such that weight average particle size is in the range of from 300 micrometers to 800 micrometers, and less than 10wt% of the agglomerates

have a particle size less than 150 micrometers and less than 10wt% of the agglomerates have a particle size greater than 1200 micrometers.

It may be preferred for fines and over-sized agglomerates to be recycled back into the agglomeration process. Typically, over-sized particles are subjected to a size reduction step, such as grinding, and recycled back into an appropriate place in the agglomeration process, such as the mixer. Typically, fines are recycled back into an appropriate place in the agglomeration process, such as the mixer.

It may be preferred for ingredients such as polymer and/or non-ionic deterative surfactant and/or perfume to be sprayed onto base detergent particles, such as spray-dried base detergent particles and/or agglomerated base detergent particles. Typically, this spray-on step is carried out in a tumbling drum mixer.

Method of laundering fabric: The method of laundering fabric comprises the step of contacting the solid composition to water to form a wash liquor, and laundering fabric in said wash liquor. Typically, the wash liquor has a temperature of above 0°C to 90°C, or to 60°C, or to 40°C, or to 30°C, or to 20°C. The fabric may be contacted to the water prior to, or after, or simultaneous with, contacting the solid composition with water. Typically, the wash liquor is formed by contacting the laundry detergent to water in such an amount so that the concentration of laundry detergent composition in the wash liquor is from 0.2g/l to 20g/l, or from 0.5g/l to 10g/l, or to 5.0g/l. The method of laundering fabric can be carried out in a front-loading automatic washing machine, top loading automatic washing machines, including high efficiency automatic washing machines, or suitable hand-wash vessels. Typically, the wash liquor comprises 90 litres or less, or 60 litres or less, or 15 litres or less, or 10 litres or less of water. Typically, 200g or less, or 150g or less, or 100g or less, or 50g or less of laundry detergent composition is contacted to water to form the wash liquor.

Dimensions: 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.”

Documents: Every document cited herein, including any cross referenced or related patent or application and any patent application or patent to which this application claims priority or benefit thereof, is hereby incorporated herein by reference in its entirety unless expressly excluded or otherwise limited. The citation of any document is not an admission that it is prior art with respect to any invention disclosed or claimed herein or that it alone, or in any

combination with any other reference or references, teaches, suggests or discloses any such invention. Further, to the extent that any meaning or definition of a term in this document conflicts with any meaning or definition of the same term in a document incorporated by reference, the meaning or definition assigned to that term in this document shall govern.

5 **Embodiments:** While particular embodiments of the present invention have been illustrated and described, it would be obvious to those skilled in the art that various other changes and modifications can be made without departing from the spirit and scope of the invention. It is therefore intended to cover in the appended claims all such changes and modifications that are within the scope of this invention.

10

EXAMPLES

Example 1: The following samples are prepared by the processes described below. Sample 3 is in accordance with the present invention. Sample 1 is a comparison sample with nil hueing
15 particle, Sample 2 is a comparison sample with nil polymer particle.

Particle 1: Hueing agent particle composition:

Ingredient	%w/w Hueing agent particle
Sodium Bentonite	83.6
Hueing agent in accordance with the structure given in claim 1.	3.8
Water	12.6

Particle 2: Polymer Particle and process of making it: An aqueous slurry composed of co-polymer in accordance with the feature (a)(i) of Claim 1, sodium sulphate, water and
20 miscellaneous ingredients was prepared at 50 °C in a crutcher making vessel. The slurry was prepared by mixing the ingredients together for least 5 minutes to ensure the slurry was homogenous.

 The slurry was then transferred by means of a rotor stator pump into a pressurized line at <3 bar and through a disintegrator. This aqueous slurry was atomized through an internally

atomized, dual fluid nozzle into a co-current spray drying tower at an air inlet temperature of 300 °C. Water was driven off and blown powder exits at the bottom of the tower into a fluid bed drier for further drying and/or agglomeration producing a solid mixture. This was then cooled to form a spray-dried powder, which is free-flowing. The spray-dried powder has a moisture content of 4.76wt%, a bulk density of 480 g/l and a median particle size range between 200-300 microns. The composition of the spray-dried powder is described below.

Ingredient	wt%
Sodium sulphate	18.67
Hydrophobically modified polyacrylate	76.57
Water	4.76

Particle 3. Spray dried particle composition:

Ingredient	Spray dried particle % w/w
Linear alkyl benzene sulphonate	18.67
Polyacrylate	3.32
Sodium carbonate	18.35
Sodium silicate 2.35R	5.71
Sodium sulphate	52.44
Water	1.30
Misc	0.21

Solid free-flowing particulate laundry detergent composition:

	Sample 1 comparison Sample, nil hue	Sample 2 comparison sample, nil polymer particle	Sample 3 in accordance with the present invention
Spray dried	11.38g	11.38g	11.38g

particle			
Polymer particle (particle 2)	0.1926g	0	0.1926g
Hueing particle (particle 1)	0	0.08g	0.08g

Example 2. Determination of depositon of hueing agent onto treated fabric: 800ml of city water (8.2 gpg, 117.26 ppm) was added to 3 glass tergotometer pots. 3g artificial soil (AS1 see below for composition) was added to each pot and stirred at 250rpm until visually dispersed.

- 5 Each sample was added to a tergotometer pot followed by 2 swatches (5 X 5 cm) of Knitted cotton or Terry Towel swatches and 4 swatches of ballast (5 X 5 cm). The mixture was stirred for 15 mins, the swatches removed and hand agitated in a beaker of city water for 10 seconds. The fabrics were squeezed by hand and and dried in electric driers for 10 mins. The above process was carried out on the same fabrics for a total of 4 times, where the wash solution was replaced
- 10 after every 2 runs). At the end of the 4th run, all fabrics were placed into the electric drier on the extra dry setting and dried until the end of the setting. Each swatch was analysed using a Polaris Spectrophotometer to measure $L^*a^*b^*$. b^* is a measure of the level of hue deposition onto fabric. The larger the negative b^* value, the greater the level of hue deposited on fabric.

AS1 Artificial soil Supplied by Equest	Weight %
Artificial Sebum	16.11
Tea (PG Tips)	7.22
Black Coffee (Nescafe)	4.44
Orange Juice (Tropicana)	13.33
Tomato Ketchup (Heinz)	14.44
Grass	5
Chocolate Baby Pudding (Heinz)	8.34
Cooking Oil (Crisp N Dry)	15.56
NTC (obtained locally in County Durham)	5.56
ETC Clay (supplied by BIC)	5.56
Hoover Dust (obtained from a local panel)	4.44

Results:

	Sample 1 comparison sample, nil hue	Sample 2 Comparison sample, nil polymer particle	Sample 3 In accordance with the present invention
Knitted Cotton b*	-13.18	-13.60	-18.84
Terry Towel b*	-11.30	-13.41	-13.70

Conclusion: sample 3 demonstrated a significantly lower b* value which indicated a higher level of hueing deposition.

5 Example 3. Solid free-flowing particulate laundry detergent composition illustrative examples:

Ingredient	Amount (in wt%)
Anionic deterative surfactant (such as alkyl benzene sulphonate, alkyl ethoxylated sulphate and mixtures thereof)	from 8wt% to 15wt%
Non-ionic deterative surfactant (such as alkyl ethoxylated alcohol)	from 0.1wt% to 4wt%
Cationic deterative surfactant (such as quaternary ammonium compounds)	from 0wt% to 4wt%
Other deterative surfactant (such as zwitterionic deterative surfactants, amphoteric surfactants and mixtures thereof)	from 0wt% to 4wt%
Carboxylate polymer (such as co-polymers of maleic acid and acrylic acid and/or carboxylate polymers comprising ether moieties and sulfonate moieties)	from 0.1wt% to 4wt%
Polyethylene glycol polymer (such as a polyethylene glycol polymer comprising polyvinyl acetate side chains)	from 0wt% to 4wt%
Polyester soil release polymer (such as Repel-o-tex and/or Texcare polymers)	from 0wt% to 2wt%
Cellulosic polymer (such as carboxymethyl cellulose, methyl cellulose and combinations thereof)	from 0.5wt% to 2wt%
Other polymer (such as care polymers)	from 0wt% to 4wt%
Zeolite builder and phosphate builder (such as zeolite 4A and/or sodium tripolyphosphate)	from 0wt% to 4wt%

Other co-builder (such as sodium citrate and/or citric acid)	from 0wt% to 3wt%
Carbonate salt (such as sodium carbonate and/or sodium bicarbonate)	from 0wt% to 20wt%
Silicate salt (such as sodium silicate)	from 0wt% to 10wt%
Filler (such as sodium sulphate and/or bio-fillers)	from 10wt% to 70wt%
Source of hydrogen peroxide (such as sodium percarbonate)	from 0wt% to 20wt%
Bleach activator (such as tetraacetylene diamine (TAED) and/or nonanoyloxybenzenesulphonate (NOBS))	from 0wt% to 8wt%
Bleach catalyst (such as oxaziridinium-based bleach catalyst and/or transition metal bleach catalyst)	from 0wt% to 0.1wt%
Other bleach (such as reducing bleach and/or pre-formed peracid)	from 0wt% to 10wt%
Photobleach (such as zinc and/or aluminium sulphonated phthalocyanine)	from 0wt% to 0.1wt%
Chelant (such as ethylenediamine-N'N'-disuccinic acid (EDDS) and/or hydroxyethane diphosphonic acid (HEDP))	from 0.2wt% to 1wt%
Hueing agent (such as direct violet 9, 66, 99, acid red 50, solvent violet 13 and any combination thereof)	from 0wt% to 1wt%
Brightener (C.I. fluorescent brightener 260 or C.I. fluorescent brightener 351)	from 0.1wt% to 0.4wt%
Protease (such as Savinase, Savinase Ultra, Purafect, FN3, FN4 and any combination thereof)	from 0.1wt% to 0.4wt%
Amylase (such as Termamyl, Termamyl ultra, Natalase, Optisize, Stainzyme, Stainzyme Plus and any combination thereof)	from 0wt% to 0.2wt%
Cellulase (such as Carezyme and/or Celluclean)	from 0wt% to 0.2wt%
Lipase (such as Lipex, Lipolex, Lipoclean and any combination thereof)	from 0wt% to 1wt%
Other enzyme (such as xyloglucanase, cutinase, pectate lyase, mannanase, bleaching enzyme)	from 0wt% to 2wt%
Fabric softener (such as montmorillonite clay and/or polydimethylsiloxane (PDMS))	from 0wt% to 15wt%
Flocculant (such as polyethylene oxide)	from 0wt% to 1wt%

Suds suppressor (such as silicone and/or fatty acid)	from 0wt% to 4wt%
Perfume (such as perfume microcapsule, spray-on perfume, starch encapsulated perfume accords, perfume loaded zeolite, and any combination thereof)	from 0.1wt% to 1wt%
Aesthetics (such as coloured soap rings and/or coloured speckles/noodles)	from 0wt% to 1wt%
Miscellaneous	balance to 100wt%

The above solid free-flowing particulate laundry detergent illustrative examples can be prepared such that the particle architecture of the detergent comprises:

Particle	wt %
AES particle	0.5% – 20%
Silicone particle	0.1% - 5%
Spray-dried particle	35% - 80%
LAS particle	1% - 30%
Hueing particle	0.1% - 5%
Polymer particle	0.1% - 5%

CLAIMS

What is claimed is:

1. A solid free-flowing particulate laundry detergent composition comprising:

(a) from 0.1wt% to 5wt% polymer particle comprising:

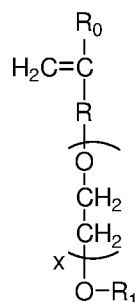
(i) from 70wt% to 90wt% co-polymer, wherein the co-polymer comprises:

(i.i) from 50 to less than 98 wt% structural units derived from one or more monomers comprising carboxyl groups;

(i.ii) from 1 to less than 49 wt% structural units derived from one or more monomers comprising sulfonate moieties; and

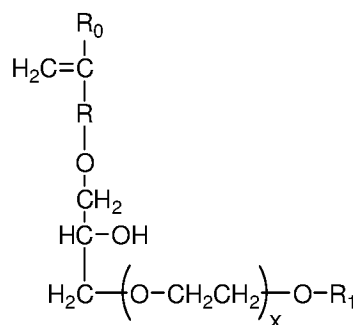
(i.iii) from 1 to 49 wt% structural units derived from one or more types of monomers selected from ether bond-containing monomers represented by formulas (I) and (II):

formula (I):



wherein in formula (I), R_0 represents a hydrogen atom or CH_3 group, R represents a CH_2 group, CH_2CH_2 group or single bond, X represents a number 0-5 provided X represents a number 1-5 when R is a single bond, and R_1 is a hydrogen atom or C_1 to C_{20} organic group;

formula (II)

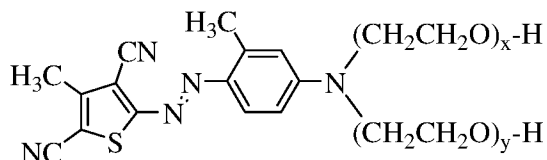


wherein in formula (II), R_0 represents a hydrogen atom or CH_3 group, R represents a CH_2 group, CH_2CH_2 group or single bond, X represents a number 0-5, and R_1 is a hydrogen atom or C_1 to C_{20} organic group; and

(ii) from 10wt% to 30wt% salt, wherein the salt is selected from sulphate salt and/or carbonate salt; and

(b) from 0.1wt% to 5wt% hueing agent particle comprising:

(i) from 2wt% to 10wt% hueing agent, wherein the hueing agent has the following structure:



wherein the index values x and y are independently selected from 1 to 10; and

(ii) from 60wt% to 98wt% clay.

2. A composition according to claim 1, wherein the composition comprises from 35wt% to 80wt% spray-dried particle comprising:

(a) from 8wt% to 24wt% alkyl benzene sulphonate anionic deterative surfactant;

(b) from 5wt% to 18wt% silicate salt;

(c) from 0wt% to 10wt% sodium carbonate; and

(d) from 0wt% to 5wt% carboxylate polymer.

3. A composition according to any preceding claim, wherein the composition comprises from 1wt% to 30wt% LAS particle comprising:

(a) from 30wt% to 50wt% alkyl benzene sulphonate anionic deterative surfactant; and

(b) from 50wt% to 70wt% salt, wherein the salt is a sodium salt and/or a carbonate salt.

4. A composition according to any preceding claim, wherein the composition comprises from 0.5wt% to 20wt% AES particle comprising:

(a) from 40wt% to 60wt% partially ethoxylated alkyl sulphate anionic deterative surfactant, wherein the partially ethoxylated alkyl sulphate anionic deterative surfactant has a molar average degree of ethoxylation of from 0.8 to 1.2, and wherein the partially ethoxylated alkyl sulphate anionic deterative surfactant has a molar ethoxylation distribution such that:

(i) from 40wt% to 50wt% is unethoxylated, having a degree of ethoxylation of 0;

(ii) from 20wt% to 30wt% has a degree of ethoxylation of 1;

(iii) from 20wt% to 40wt% has a degree of ethoxylation of 2 or greater;

(b) from 20wt% to 50wt% salt, wherein the salt is selected from sulphate salt and/or carbonate salt; and

(c) from 10wt% to 30wt% silica.

5 5. A composition according to any preceding claim, wherein the composition comprises from 0.1wt% to 5wt% silicone particle comprising:

(a) from 10wt% to 20wt% silicone; and

(b) from 50wt% to 80wt% carrier.

10 6. A composition according to any preceding claim, wherein the composition comprises:

(a) from 0wt% to 5wt% zeolite builder;

(b) from 0wt% to 5wt% phosphate builder; and

(c) from 0wt% to 5wt% sodium carbonate.

15 7. A composition according to any preceding claim, wherein the polymer particle is a spray-dried particle.

8. A composition according to any preceding claim, wherein the polymer particle comprises from 10wt% to 30wt% sodium sulphate salt.

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9. A composition according to any preceding claim, wherein the hueing agent particle comprises montmorillonite clay.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2016/025448

A. CLASSIFICATION OF SUBJECT MATTER

INV. C11D3/04 C11D3/10 C11D3/12 C11D3/37 C11D3/40
C11D17/06

ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2008/087497 A1 (PROCTER & GAMBLE [US]) 24 July 2008 (2008-07-24) page 2, lines 9-17 page 4, line 7 - page 6, line 10 page 33; examples 1-3; table 1A page 44; table 7 page 48, lines 4-10 claims	1-9
A	WO 2013/169536 A1 (MILLIKEN & CO [US]) 14 November 2013 (2013-11-14) page 1, lines 11-17 page 22, line 24 - page 23, line 11 examples 1, 2, 4 ----- -/--	1-9



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search

27 May 2016

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Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Bertran Nadal, Josep

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2016/025448

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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A	WO 2014/040010 A2 (PROCTER & GAMBLE [US]) 13 March 2014 (2014-03-13) page 24, line 27 - page 25, line 9 example 5; table 3 claims 1, 17 -----	1-9
A	WO 2015/003638 A1 (PROCTER & GAMBLE [US]) 15 January 2015 (2015-01-15) claims 1, 3, 4; examples -----	1-9
A	US 2014/366281 A1 (MORT III PAUL R [CN] ET AL) 18 December 2014 (2014-12-18) paragraphs [0001], [0006], [0029] examples 2, 3; table IV claims -----	1-9
A	EP 2 581 438 A1 (PROCTER & GAMBLE [US]) 17 April 2013 (2013-04-17) paragraphs [0005], [0013], [0017] - [0021] examples claims -----	1-9

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International application No

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