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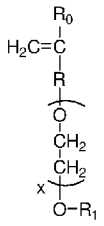
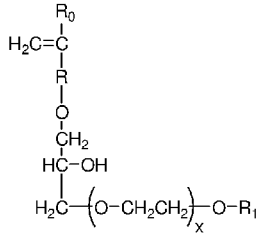
(54) Title: A SPRAY-DRIED LAUNDRY DETERGENT BASE PARTICLE

(57) Abstract: The present invention relates to a spray-dried laundry base detergent particle comprising: (a) from 8wt% to 35wt% detersive surfactant; (b) from 56wt% to 91.49wt% sulphate salt; (c) from 0.3wt% to 5wt% carboxylate co-polymer, wherein 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): formula (I): wherein in formula (I), R_0 represents a hydrogen atom or CH_3 group, R represents a CH_2group,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; (d) from 0.01wt% to 1wt% water; (e) from 0wt% to 3wt% silicate salt; (f) from 0wt% to 3wt% zeolite; (g) from 0wt% to 3wt% phosphate salt; and (h) from 0wt% to 3wt% sodium carbonate.

(I)



(II)



WO 2016/160863 A1

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A SPRAY-DRIED LAUNDRY DETERGENT BASE PARTICLE

FIELD OF THE INVENTION

The present invention relates to a spray-dried laundry detergent base particle.

BACKGROUND OF THE INVENTION

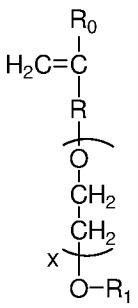
Recent consumer trends have moved the laundry detergent industry to colder washing temperatures and shorter washing cycles. To meet these consumer needs, detergent manufacturers seek to provide laundry detergent powders having an excellent solubility profile, low fabric residue profile, good hand-feel profile and good cleaning profile. Removing or reducing the levels of ingredients such as zeolite, silicate and carbonate from the detergent base powder, such as the spray-dried particle, improves the solubility, fabric residue and hand feel performance of the laundry detergent powder. In addition, reducing or removing phosphate improves the environmental profile of the laundry detergent powder. However, laundry detergent powders having no, or low levels of, zeolite, carbonate, silicate and phosphate in the base detergent particle have poor physical characteristics, such as high cake strength which can lead of caking of the powder during storage and consumer use.

The Inventors have found that the addition of a specific polymer to a spray-dried base detergent particle having low, or no, levels of carbonate, zeolite, phosphate and silicate results in an improvement in the physical characteristics of the particle whilst preserving its excellent solubility, low fabric residue and good hand feel profile.

SUMMARY OF THE INVENTION

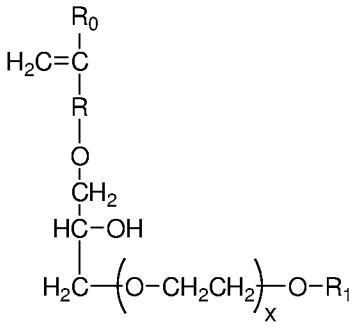
The present invention provides a spray-dried laundry base detergent particle comprises: (a) from 8wt% to 35wt% detersive surfactant; (b) from 56wt% to 91.49wt% sulphate salt; (c) from 0.3wt% to 5wt% carboxylate co-polymer, wherein the co-polymer comprises: (i) from 50 to less than 98 wt% structural units 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):

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)



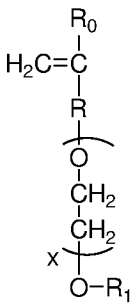
wherein in formula (II), R_0 represents a hydrogen atom or CH_3 group, R represents a CH_2 group, CH_2CH_2 group or single bond, X represents a number 0-5, and R_1 is a hydrogen atom or C_1 to C_{20} organic group; (d) from 0.01wt% to 1wt% water; (e) from 0wt% to 3wt% silicate salt; (f) from 0wt% to 3wt% zeolite; (g) from 0wt% to 3wt% phosphate salt; and (h) from 0wt% to 3wt% sodium carbonate.

DETAILED DESCRIPTION OF THE INVENTION

Spray-dried laundry base detergent particle: The spray-dried laundry base detergent particle comprises: (a) from 8wt% to 35wt% detersive surfactant; (b) from 56wt% to 91.49wt% sulphate salt; (c) from 0.3wt% to 5wt% carboxylate co-polymer, wherein 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

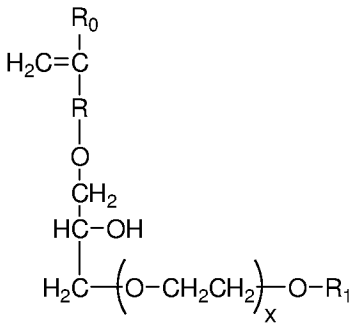
derived from one or more types of monomers selected from ether bond-containing monomers represented by formulas (I) and (II):

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)

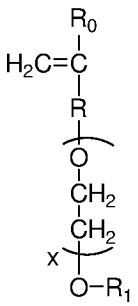


wherein in formula (II), R_0 represents a hydrogen atom or CH_3 group, R represents a CH_2 group, CH_2CH_2 group or single bond, X represents a number 0-5, and R_1 is a hydrogen atom or C_1 to C_{20} organic group; (d) from 0.01wt% to 1wt% water; (e) from 0wt% to 3wt% silicate salt; (f) from 0wt% to 3wt% zeolite; (g) from 0wt% to 3wt% phosphate salt; and (h) from 0wt% to 3wt% sodium carbonate.

Preferably, the particle comprises: (a) from 8wt% to 20wt% alkyl benzene sulphonate; (b) from 81.5wt% to 91.49wt% sodium sulphate; (c) from 0.3wt% to 2wt% carboxylate co-polymer, wherein 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

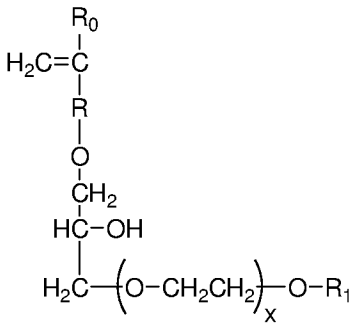
units derived from one or more monomers comprising sulfonate moieties; and (iii) from 1 to 49 wt% structural units derived from one or more types of monomers selected from ether bond-containing monomers represented by formulas (I) and (II):

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 wherein the co-polymer has a weight average molecular weight of at least 50kDa; (d) from 0.01wt% to 0.5wt% water; (e) wherein the particle is essentially free of silicate salt; (f) wherein the particle is essentially free of zeolite; and (g) wherein the particle is essentially free of phosphate salt; and (h) essentially free of sodium carbonate.

Preferably, the particle has a bulk density in the range of from 350g/l to 550g/l.

Preferably, the particle has a weight average particle size in the range of from 300 micrometers to 600 micrometers, and a particle size distribution such that no more than 15wt% have a particle size of less than 100 micrometers, and no more than 15wt% of the particles have a particle size of greater than 1180 micrometers.

Preferably, the particle has a cake strength of less than 8N, preferably less than 6N.

Preferably, the particle comprises from above 0wt to 2wt% sodium silicate having a SiO_2:NaO ratio of from 2.00 to 2.35.

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.

Solid free-flowing particulate laundry detergent composition: The spray-dried laundry base detergent particle is typically incorporated into a solid free-flowing particulate laundry detergent composition. Typically, this is achieved by mixing the spray-dried laundry base detergent particle with other detergent particles.

The solid particulate free-flowing laundry detergent composition typically comprises: (a) from 30wt% to 85wt% spray-dried laundry base detergent particle according to any preceding claim; (b) from 0wt% to 3wt% silicate salt; (c) from 0wt% to 3wt% zeolite; and (d) from 0wt% to 3wt% phosphate salt.

Preferably, the composition is essentially free of silicate salt and essentially free of phosphate salt.

Preferably, the composition comprises an additional detersive surfactant selected from the group consisting of: alkylethoxy sulphate; alkylethoxy alcohol; and a combination thereof.

Preferably, the composition comprises a separate detersive surfactant particle comprising alkylbenzene sulphonate.

Preferably, the composition comprises a hueing dye.

Preferably, the composition comprises an enzyme selected from protease, amylase, cellulase, lipase, and any combination thereof.

Preferably, the composition comprises a source of hydrogen peroxide and a bleach activator.

Preferably, the composition comprises a perfume microcapsule.

Preferably, the composition comprises an LAS particle, AES particle, silicone particle and hueing agent particle. These particles are described in more detail below.

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 the spray-dried base detergent particle of the present invention, optionally in combination with another base detergent particle such agglomerated base detergent particles and/or extruded base detergent particles. The base detergent particle is typically combined 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.

LAS particle: The LAS particle comprises: (a) from 30wt% to 50wt% alkyl benzene sulphonate anionic detersive 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 detersive 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 detersive surfactant, wherein the partially ethoxylated alkyl sulphate anionic detersive surfactant has a molar average degree of ethoxylation of from 0.8 to 1.2, and wherein the partially ethoxylated alkyl sulphate anionic detersive 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 20% to 40% 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 detersive 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 detersive 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 rario 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.

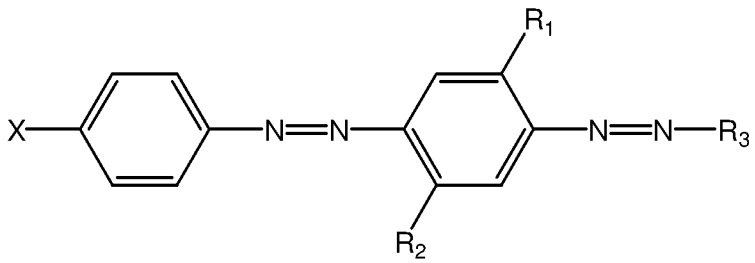
Typically, the ethoxylated alkyl alcohol is sulphated in a falling film reactor with SO_3 to form a surfactant acid precursor, which is then neutralized with NaOH to form the ethoxylated alkyl sulphate anionic detersive surfactant (AES).

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 pKb $\leq$ 5, more preferably with a pKb $\leq$ 3, more preferably with a pKb $\leq$ 1, most preferably with a pKb $\leq$ 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 detersive surfactant, salt and silica are dosed into one or more mixers and agglomerated to form the AES particle.

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



wherein: R1 and R2 are independently selected from the group consisting of: H; alkyl; alkoxy; alkyleneoxy; alkyl capped alkyleneoxy; urea; and amido; R3 is a substituted aryl group; X is a substituted group comprising sulfonamide moiety and optionally an alkyl and/or aryl moiety, and wherein the substituent group comprises at least one alkyleneoxy chain that comprises an average molar distribution of at least four alkyleneoxy moieties; and (b) from 90wt% to 98wt% clay. Preferably, the clay is a montmorillonite clay, also known as bentonite clay.

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: Suitable laundry detergent compositions comprise a detergent ingredient selected from: detersive surfactant, such as anionic detersive surfactants, non-ionic detersive surfactants, cationic detersive surfactants, zwitterionic detersive surfactants and amphoteric detersive 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 supressors; and any combination thereof.

Suitable laundry detergent compositions may have a low buffering capacity. Such laundry detergent compositions typically have a reserve alkalinity to pH 9.5 of less than 5.0gNaOH/100g. These low buffered laundry detergent compositions typically comprise low levels of carbonate salt.

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

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

Suitable sulphonate detersive surfactants include methyl ester sulphonates, alpha olefin sulphonates, alkyl benzene sulphonates, especially alkyl benzene sulphonates, preferably C_{10-13} 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 supplied by Sasol under the tradename Hyblene®.

Suitable sulphate detersive surfactants include alkyl sulphate, preferably C_{8-18} alkyl sulphate, or predominantly C_{12} alkyl sulphate.

A preferred sulphate detersive surfactant is alkyl alkoxylated sulphate, preferably alkyl ethoxylated sulphate, preferably a C_{8-18} alkyl alkoxylated sulphate, preferably a C_{8-18} alkyl ethoxylated sulphate, preferably the alkyl alkoxylated sulphate has an average degree of alkoxylation of from 0.5 to 20, preferably from 0.5 to 10, preferably the alkyl alkoxylated sulphate is a C_{8-18} alkyl ethoxylated 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.

The alkyl sulphate, alkyl alkoxylated 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 detersive surfactants include alkyl ether carboxylates.

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

Non-ionic detersive surfactant: Suitable non-ionic detersive surfactants are selected from the group consisting of: C_8-C_{18} alkyl ethoxylates, such as, NEODOL® non-ionic surfactants from Shell; C_6-C_{12} alkyl phenol alkoxylates wherein preferably the alkoxylate units are ethyleneoxy units, propyleneoxy units or a mixture thereof; C_{12}-C_{18} alcohol and C_6-C_{12} 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 detersive surfactants are alkylpolyglucoside and/or an alkyl alkoxylated alcohol.

Suitable non-ionic detersive surfactants include alkyl alkoxylated alcohols, preferably C_{8-18} alkyl alkoxylated alcohol, preferably a C_{8-18} alkyl ethoxylated alcohol, preferably the alkyl alkoxylated 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 alkoxylated alcohol is a C_{8-18} 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 alkoxylated alcohol can be linear or branched, and substituted or un-substituted.

Suitable nonionic detersive surfactants include secondary alcohol-based detersive surfactants.

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

Preferred cationic detersive surfactants are quaternary ammonium compounds having the general formula:

$$(R)(R_1)(R_2)(R_3)N^+ X^-$$

wherein, R is a linear or branched, substituted or unsubstituted C_{6-18} alkyl or alkenyl moiety, R_1 and R_2 are independently selected from methyl or ethyl moieties, R_3 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.

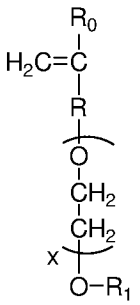
Zwitterionic detersive surfactant: Suitable zwitterionic detersive surfactants include amine oxides and/or betaines.

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.

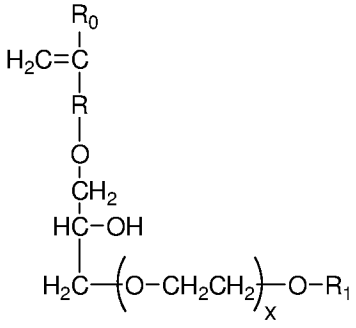
Another suitable carboxylate polymer is a co-polymer that comprises: (i) from 50 to less than 98 wt% structural units derived from one or more monomers comprising carboxyl groups; (ii) from 1 to less than 49 wt% structural units derived from one or more monomers comprising sulfonate moieties; and (iii) 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):

(I) $-[(OCHR^1\text{-}CHR^2)_a\text{-}O\text{-}OC\text{-}Ar\text{-}CO\text{-}]_d$

(II) $-[(OCHR^3\text{-}CHR^4)_b\text{-}O\text{-}OC\text{-}sAr\text{-}CO\text{-}]_e$

(III) $-[(OCHR^5\text{-}CHR^6)_c\text{-}OR^7]_f$

wherein:

a, b and c are from 1 to 200;

d, e and f are from 1 to 50;

Ar is a 1,4-substituted phenylene;

sAr is 1,3-substituted phenylene substituted in position 5 with SO_3Me;

Me is Li, K, Mg/2, Ca/2, Al/3, ammonium, mono-, di-, tri-, or tetraalkylammonium wherein the alkyl groups are C_1-C_{18} alkyl or C_2-C_{10} hydroxyalkyl, or mixtures thereof;

R^1, R^2, R^3, R^4, R^5 and R^6 are independently selected from H or C_1-C_{18} n- or iso-alkyl; and

R^7 is a linear or branched C_1-C_{18} alkyl, or a linear or branched C_2-C_{30} alkenyl, or a cycloalkyl group with 5 to 9 carbon atoms, or a C_8-C_{30} aryl group, or a C_6-C_{30} 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® 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) selected from the group consisting of: C_4-C_{25} alkyl group, polypropylene, polybutylene, vinyl ester of a saturated C_1-C_6 mono-carboxylic acid, C_1-C_6 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, sulphoalkyl cellulose, more preferably selected from carboxymethyl cellulose, methyl cellulose, methyl hydroxyethyl cellulose, methyl carboxymethyl cellulose, and mixures 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).

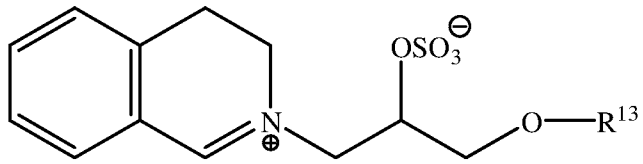
Other suitable care polymers include amino-silicone, which can provide fabric feel benefits and fabric shape retention benefits.

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, transistion 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-pentylnonyl, 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®, Liquanase®, Liquanase Ultra®, Savinase Ultra®, Ovozyme®, 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 folowing 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, Optisize® HT Plus (all Du Pont).

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 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 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*).

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.

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 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 $Na_2O:SiO_2$ 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-napthol[1,2-d]triazole, disodium 4,4'-bis{[(4-anilino-6-(N methyl-N-2 hydroxyethyl)amino 1 ,3,5- triazin-2-yl)];amino}stilbene-2-2' 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 alkoxylated. Such alkoxylated 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 alkoxylated bis-azo dyes, such as described in WO2012/054835, and/or alkoxylated 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, polyvinyloxazolidone, 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 detersive ingredient, such as a detersive 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 detersive 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 detersive surfactant is neutralized by the alkaline material to form a detersive 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 detersive 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.

Method for measuring cake strength: Cake strength can be measured by the following method. A smooth plastic cylinder of internal diameter 6.35 cm and length 15.9 cm is supported on a suitable base plate. A 0.65 cm hole is drilled through the cylinder with the centre of the hole being 9.2cm from the end opposite the base plate.

A metal pin is inserted through the hole and a smooth plastic sleeve of internal diameter 6.35cm and length 15.25 cm is placed around the inner cylinder such that the sleeve can move freely up and down the cylinder and comes to rest on the metal pin. The space inside the sleeve is then filled (without tapping or excessive vibration) with the spray-dried powder such that the spray-dried powder is level with the top of the sleeve. A lid is placed on top of the sleeve and a 5 kg weight placed on the lid. The pin is then pulled out and the spray-dried powder is allowed to compact for 2 minutes. After 2 minutes the weight is removed, the sleeve is lowered to expose the powder cake with the lid remaining on top of the powder.

A metal probe is then lowered at 54 cm/min such that it contacts the centre of the lid and breaks the cake. The maximum force required to break the cake is recorded and is the result of the test. A cake strength of 0 N refers to the situation where no cake is formed.

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.

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.

EXAMPLES

Six aqueous slurry (S1, S2, S3, S4, S5, S6) having the composition as described below in table A were prepared to a moisture content of 35.0 %. All aqueous slurries is heated to 50°C and pumped under high pressure (from 5.5 x $10^6 Nm^{-2}$ to 6 x$10^6 Nm^{-2}$), into a spray-drying tower with an air inlet temperature of from 280 °C. The six aqueous slurry are in the spray dryer and dried to produce respectively six spray dried powder produced with an average mean particle in range 300 – 360 microns to form a spray-dried powder. All spray-dried powders are dried to moisture of 0.3 wt%. Powder bulk densities range from 450 to 500 g/l. The composition of the spray-dried powders are summarized in table B below with slurry S1 producing BP1 composition, S2 producing BP2, S3 producing BP3, S4 producing BP4, S5 producing BP5 and S6 producing BP6.

Table A	**% w/w Aqueous slurry – RM constituent parts**					
Component	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**
Polymer Type	Standard Acylate/maleate co polymer	Hydrophobic Polymer – 38 kD	Hydrophobic Polymer – 50 kD	Standard Polyacrylate	Hydrophobic Polymer – 38 kD	Hydrophobic Polymer – 50 kD
Linear alkyl benzene sulphonate	12.72	12.72	12.72	12.81	12.81	12.81
Polymer Level	0.26	0.26	0.26	1.97	1.97	1.97
Sodium Sulphate	51.38	51.38	51.38	49.58	49.58	49.58
Water	35.00	35.00	35.00	35.00	35.00	35.00
Miscellaneous	0.64	0.64	0.64	0.64	0.64	0.64
Total	100.00	100.00	100.00	100.00	100.00	100.00

Table B	**% w/w Blown Powder – RM constituent parts**					
Component	**BP1**	**BP2**	**BP3**	**BP4**	**BP5**	**BP6**
Polymer Type	Standard	Hydrophobi	Hydrophobi	Standard	Hydrophobi	Hydrophobi

	Acylate/maleate co polymer	c Polymer – 38 kD	c Polymer – 50 kD	Polyacrylate	c Polymer – 38 kD	c Polymer – 50 kD
Linear alkyl benzene sulphonate	19.50	19.50	19.50	19.50	19.50	19.50
Polymer Level	0.40	0.40	0.40	3.00	3.00	3.00
Sodium Sulphate	78.78	78.78	78.78	76.18	76.18	76.18
Water	0.30	0.30	0.30	0.3	0.3	0.3
Miscellaneous	1.02	1.02	1.02	1.02	1.02	1.02
Total	100.00	100.00	100.00	100.00	100.00	100.00

Powders BP1, BP2, BP3, BP4, BP5 and BP6 are collected from the spray dryer and analysed for cake strength. Cake strength data for BP1, BP2 and BP3 are summarized in table C. Cake strength data for BP4, BP5 and BP6 are summarized in table D. The six powder combination test for effective cake strength control at (i) 2 polymer levels (0.4 % wt, 3 % wt) and (ii) 3 different polymer types; standard acylate/maleate co polymer, hydrophobically modified polyacrlate at 38 k Daltons Average Molecular Weight and hydrophobically modified polyacrlate at 50 k Daltons Average Molecular Weight.

Cake Strength Results – 0.4 % wt polymer in Spray Dried Blown Granules

Table C		**Spray Dried Powder Cake Strength (Newtons)**
BP1	Acylate/maleate co polymer	10.8
BP2	Hydrophobically Modified Polymer 38k Molecular Weight	7.8
BP3	Hydrophobically Modified Polymer 50k Molecular Weight	5.9

Cake Strength Results – 3.0 % wt polymer in Spray Dried Blown Granules

Table D		**Spray Dried Powder Cake Strength (Newton)**
BP4	Acylate/maleate co polymer	14.7
BP5	Hydrophobically Modified Polymer 38k Molecular Weight	0 (cake not formed)
BP6	Hydrophobically Modified Polymer 50k Molecular Weight	0 (cake not formed)

Conclusions: Table C results show the lowering in cake strength of spray dried granules with hydrophobically modified polymers over the acylate / maleate co polymer. Further lowering in cake strength is observed when higher average molecular weight of the hydrophobic modified polymer is used.

Table D results show cake strength of spray dried granules at high polymer levels. Although no measureable lowering in cake strength is observed at higher levels of acylate / maleate co polymer, a significant lower in cake strength is observed for both hydrophobic polymers to the point that neither BP5 nor BP6 produces a stable cake after pre consolidation.

Solid free-flowing particulate laundry detergent composition illustrative examples:

Ingredient	**Amount (in wt%)**
Anionic detersive surfactant (such as alkyl benzene sulphonate, alkyl ethoxylated sulphate and mixtures thereof)	from 8wt% to 15wt%
Non-ionic detersive surfactant (such as alkyl ethoxylated alcohol)	from 0.1wt% to 4wt%
Cationic detersive surfactant (such as quaternary ammonium compounds)	from 0wt% to 4wt%
Other detersive surfactant (such as zwiterionic detersive surfactants, amphoteric surfactants and mixtures thereof)	from 0wt% to 4wt%
Carboxylate polymer (such as co-polymers of maleic acid	from 0.1wt% to 4wt%

and acrylic acid and/or carboxylate polymers comprising ether moieties and sulfonate moieties)	
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 3wt%
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 3wt%
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 tetraacetylethylene 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%

CLAIMS

What is claimed is:

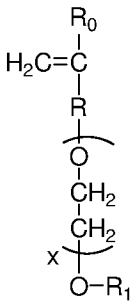
1. A Spray-dried laundry base detergent particle comprising:

(a) from 8wt% to 35wt% detersive surfactant;

(b) from 56wt% to 91.49wt% sulphate salt;

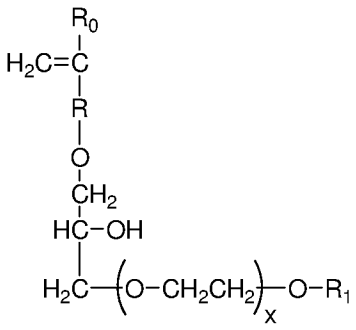
(c) from 0.3wt% to 5wt% carboxylate co-polymer, wherein the co-polymer comprises: (i) from 50 to less than 98 wt% structural units derived from one or more monomers comprising carboxyl groups; (ii) from 1 to less than 49 wt% structural units derived from one or more monomers comprising sulfonate moieties; 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):

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;

(d) from 0.01wt% to 1wt% water;

(e) from 0wt% to 3wt% silicate salt;

(f) from 0wt% to 3wt% zeolite;

(g) from 0wt% to 3wt% phosphate salt; and

(h) from 0wt% to 3wt% sodium carbonate.

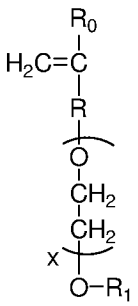
2. A Spray-dried laundry base detergent particle according to claim 1, wherein the particle comprises:

(a) from 8wt% to 20wt% alkyl benzene sulphonate;

(b) from 81.5wt% to 91.49wt% sodium sulphate;

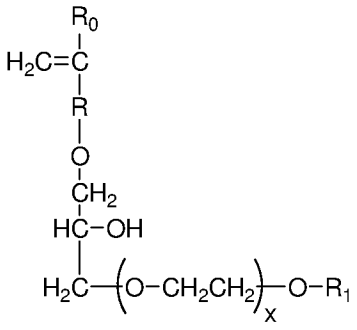
(c) from 0.3wt% to 2wt% carboxylate co-polymer, wherein the co-polymer comprises: (i) from 50 to less than 98 wt% structural units derived from one or more monomers comprising carboxyl groups; (ii) from 1 to less than 49 wt% structural units derived from one or more monomers comprising sulfonate moieties; 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):

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 wherein the co-polymer has a weight average molecular weight of at least 50kDa;

(d) from 0.01wt% to 0.5wt% water;

(e) essentially free of silicate salt;

(f) essentially free of zeolite; and

(g) essentially free of phosphate salt; and

(h) essentially free of sodium carbonate.

3. A spray-dried laundry base detergent particle according to any preceding claim, wherein the particle has a bulk density in the range of from 350g/l to 550g/l.

4. A spray-dried laundry base detergent particle according to any preceding claim, wherein the particle has a weight average particle size in the range of from 300 micrometers to 600 micrometers, and a particle size distribution such that no more than 15wt% have a particle size of less than 100 micrometers, and no more than 15wt% of the particles have a particle size of greater than 1180 micrometers.

5. A spray-dried laundry base detergent particle according to any preceding claim, wherein the particle has a cake strength of less than 8N, preferably less than 6N.

6. A spray-dried laundry base detergent particle according any of claims 1 and 3-5, wherein the particle comprises from above 0wt to 2wt% sodium silicate having a SiO_2:NaO ratio of from 2.00 to 2.35.

7. A solid particulate free-flowing laundry detergent composition comprising:
(a) from 30wt% to 85wt% spray-dried laundry base detergent particle according to any preceding claim;
(b) from 0wt% to 3wt% silicate salt;
(c) from 0wt% to 3wt% zeolite; and
(d) from 0wt% to 3wt% phosphate salt.

8. A solid composition according to claim 7, wherein the composition is essentially free of silicate salt and essentially free of phosphate salt.

9. A solid composition according to any of claims 7-8, wherein the composition comprises an additional detersive surfactant selected from the group consisting of: alkylethoxy sulphate; alkylethoxy alcohol; and a combination thereof.

10. A solid composition according to any of claims 7-9, wherein the composition comprises a separate detersive surfactant particle comprising alkylbenzene sulphonate.

11. A solid composition according to any of claims 7-10, wherein the composition comprises a hueing dye.

12. A solid composition according to any of claims 7-11, wherein the composition comprises an enzyme selected from protease, amylase, cellulase, lipase, and any combination thereof.

13. A solid composition according to any of claims 7-12, wherein the composition comprises a source of hydrogen peroxide and a bleach activator.

14. A solid composition according to any of claims 7-13, wherein the composition comprises a perfume microcapsule.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2016/024813

A. CLASSIFICATION OF SUBJECT MATTER
INV. C11D1/22 C11D3/04 C11D3/37 C11D11/02 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.
X	EP 2 801 606 A1 (PROCTER & GAMBLE [US]) 12 November 2014 (2014-11-12) paragraphs [0001], [0011] - [0017], [0023], [0036] paragraph [0071]; example; table 2 claims -----	1-14
A	EP 2 669 361 A1 (PROCTER & GAMBLE [US]) 4 December 2013 (2013-12-04) paragraphs [0005], [0007], [0014], [0025] - [0030], [0035], [0048] examples; table 3 claims -----	1-14

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
25 May 2016	01/06/2016

Name and mailing address of the ISA/	Authorized officer
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1

Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 2 801 609 A1 (PROCTER & GAMBLE [US]) 12 November 2014 (2014-11-12) paragraphs [0005], [0006], [0013], [0014], [0028] - [0035], [0052] example; table 3 claims	1-14
A	WO 2014/040010 A2 (PROCTER & GAMBLE [US]) 13 March 2014 (2014-03-13) page 24, line 27 - page 25, line 9 claims 1, 17	1-14
A	WO 2015/003638 A1 (PROCTER & GAMBLE [US]) 15 January 2015 (2015-01-15) claims 1, 3, 4	1-14
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	1-14

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2016/024813

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 2801606 A1	12-11-2014	CN 105164240 A	16-12-2015
		EP 2801606 A1	12-11-2014
		WO 2014182417 A1	13-11-2014
EP 2669361 A1	04-12-2013	CN 104350140 A	11-02-2015
		EP 2669361 A1	04-12-2013
		ES 2534823 T3	29-04-2015
		JP 2015525257 A	03-09-2015
		US 2013324452 A1	05-12-2013
		WO 2013181340 A1	05-12-2013
EP 2801609 A1	12-11-2014	EP 2801609 A1	12-11-2014
		WO 2014182416 A1	13-11-2014
WO 2014040010 A2	13-03-2014	CN 104640966 A	20-05-2015
		EP 2892988 A2	15-07-2015
		US 2014073551 A1	13-03-2014
		WO 2014040010 A2	13-03-2014
WO 2015003638 A1	15-01-2015	US 2015018263 A1	15-01-2015
		WO 2015003362 A1	15-01-2015
		WO 2015003638 A1	15-01-2015
WO 2013169536 A1	14-11-2013	CA 2869626 A1	14-11-2013
		CN 104302752 A	21-01-2015
		EP 2847309 A1	18-03-2015
		JP 2015516023 A	04-06-2015
		US 2013303428 A1	14-11-2013
		WO 2013169536 A1	14-11-2013