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(54) **DETERGENT GRANULES WITH HIGH ANIONIC SURFACTANT CONTENT**

WASCHMITTELGRANULATE MIT HOHEM ANIONTENSIDEGEHALT

GRANULÉS DÉTERGENTS AYANT UNE TENEUR EN TENSIOACTIF ANIONIQUE ÉLEVÉE

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Description

FIELD OF THE INVENTION

5 **[0001]** This invention relates to detergent granules with a relatively high total anionic surfactant content for use in granular detergent compositions.

BACKGROUND OF THE INVENTION

10 **[0002]** Granular detergent compositions of today are trending more and more toward high compaction, which enables a myriad of benefits including superior cleaning, environmental sustainability, convenience and efficiency. Such high compaction granular detergent compositions are formed by detergent granules with high concentrations of cleaning actives or surfactants, especially those with high concentrations of anionic surfactants and blends thereof.

15 **[0003]** Currently, the desired surfactant concentration may be as high as 40% to 90%, preferably 50% to 80%, by total weight of the detergent granules. However, there are challenges in both manufacturing and end-use of products comprising detergent granules with such high surfactant concentrations, especially if the surfactants are mainly anionic surfactants. First, when anionic surfactants are the dominant components in the detergent granules, the physical strength of the detergent granules is significantly worsened in comparison with detergent granules with lower anionic surfactant contents. Second, the granule surface is significantly stickier. Both factors contribute to poor flowability of the resulting granules, which in turn leads to challenges in bulk-handling of such detergent granules during the manufacturing process.

20 **[0004]** There is therefore a continuing need to improve the flowability of highly concentrated anionic detergent granules without reducing the anionic surfactant concentrations therein.

[0005] US 2015/291913 A1 relates to a composite detergent granule having a core particle covered by a coating layer.

25 **[0006]** WO 00/05334 A1 relates to a laundry detergent composition which includes an anionic surfactant system including a linear alkylbenzene sulfonate and an alkyl sulfate, and the combination of a certain modified polyethyleneimine polymer and a stilbenedisulfonate brightener to provide improved dye transfer inhibition.

SUMMARY OF THE INVENTION

30 **[0007]** The present invention discovered, surprisingly and unexpectedly, that the addition of a non-quaternized alkoxylated polyethyleneimine into detergent granules of high anionic surfactant concentrations and the formation of a silica coating layer thereover can significantly increase the flowability of such detergent granules.

[0008] In one aspect, the present invention relates to a detergent granule that is characterized by a total anionic surfactant content ranging from 40% to 90% by weight. Specifically, such detergent granule contains:

35 a core that contains: (a) one or more anionic surfactants; and (b) a non-quaternized alkoxylated polyethyleneimine having a polyalkyleneimine core with one or more alkoxy side chains bonded to at least one nitrogen atom in the polyalkyleneimine core; and a coating layer over the core, while such coating layer contains silica.

Another aspect not according to the invention relates to a detergent granule containing:

40 a core that contains: (i) from about 40% to about 9%, by total weight of the detergent granule, of a C₁₂-C₁₄ linear alkylethoxylated sulfate (AES) surfactant having a weight average degree of ethoxylation of from about 0.5 to about 1; (ii) from about 10% to about 50%, by total weight of the detergent granule, of a C₁₂-C₁₄ linear alkyl benzene sulphonate (LAS) surfactant; (iii) from about 1% to about 10%, by total weight of the detergent granule, of a non-quaternized alkoxylated polyethyleneimine having an empirical formula (I) of (PEI)_x-(EO)_y-R₃, while x is the average number-average molecular weight of the polyalkyleneimine core (MWPEI) of the alkoxylated polyalkyleneimine and is in the range of from about 500 to about 1000 Daltons, while y is the weight average degree of ethoxylation in said one or more side chains of the alkoxylated polyalkyleneimine and is in the range of from about 10 to about 30, and while R₃ is hydrogen; and (iv) from about 20% to about 40%, by total weight of the detergent granule, of silica; and a coating layer over the core, while such coating layer contains from about 1% to about 10%, by total weight of the detergent granule, of silica.

[0009] In yet another aspect, the present invention relates to a granular detergent composition containing from about 1% to about 99% of the above-described detergent granule.

55 **[0010]** In still another aspect, the present invention relates to a method of making the above-described detergent granule, by: (a) forming aqueous paste comprising the one or more anionic surfactants, the non-quaternized alkoxylated polyethyleneimine, and water; (b) mixing the aqueous paste from step (a) with a solid carrier to form a core particle; and (c) coating silica over the core particle.

[0011] These and other aspects of the present invention will become more apparent upon reading the following drawings

and detailed description of the invention.

DETAILED DESCRIPTION OF THE INVENTION

[0012] Features and benefits of the various embodiments of the present invention will become apparent from the following description, which includes examples of specific embodiments intended to give a broad representation of the invention.

[0013] The terms "include", "includes" and "including" are meant to be non-limiting.

[0014] As used herein, the term "granule" or "particle" refers to a solid matter of minute quantity, such as a powder, granule, encapsulate, microcapsule, and/or prill. The granules or particles of the present invention can be spheres, rods, plates, tubes, squares, rectangles, discs, stars or flakes of regular or irregular shapes, but they are non-fibrous. The granules or particles of the present invention may have a median particle size of about 2000 μm or less, as measured according to the Median Particle Size Test described herein. Preferably, the particles of the present invention have a median particle size ranging from about 1 μm to about 2000 μm , more preferably from about 10 μm to about 1800 μm , still more preferably from about 50 μm to about 1700 μm , still more preferably from about 100 μm to about 1500 μm , still more preferably from about 250 μm to about 1000 μm , most preferably from about 300 μm to about 800 μm , as measured according to the Median Particle Size Test described herein.

[0015] As used herein, the term "composite detergent granule," "composite detergent particle," "hybrid detergent granule," or "hybrid detergent particle" refer to granules or particles containing two or more surfactants, preferably at least two anionic surfactants.

[0016] As used herein, the term "main surfactant" refers to a surfactant which is present in an article at an amount of about 50% or more, by total weight of all surfactants in such article.

[0017] As used herein, the term "coating layer" means a partial or complete coating of a layering material over the outer surfaces of a particulate or granular material, or at least a portion of such outer surfaces.

[0018] As used herein, the term "a granular detergent composition" refers to a solid composition, such as granular or powder-form all-purpose or heavy-duty washing agents, e.g., for cleaning fabrics, dishes, and/or hard surface, as well as cleaning auxiliaries such as bleach, rinse aids, additives, or pre-treat types.

[0019] As used herein, the term "water-soluble" refers to the ability of a sample material to completely dissolve in or disperse into water leaving no visible solids or forming no visibly separate phase, when at least about 25 grams, preferably at least about 50 grams, more preferably at least about 100 grams, most preferably at least about 150 grams, of such material is placed in one liter (1L) of deionized water at 20°C and under the atmospheric pressure with sufficient stirring.

[0020] As used herein, the term "substantially free of" means that the component of interest is present in an amount less than about 0.1% by weight.

[0021] As used herein, the terms "consisting essentially of" means that the composition contains no ingredient that will interfere with benefits or functions of those ingredients that are explicitly disclosed. Further, the term "substantially free of" or "substantially free from" means that the indicated material is present in the amount of from 0 wt% to about 5 wt%, preferably from 0 wt% to 3 wt%. The term "essentially free of" means that the indicated material is present in the amount of from 0 wt% to about 1 wt%, preferably from 0 wt% to about 0.5 wt%, more preferably from 0 wt% to about 0.1 wt%, most preferably it is not present at analytically detectable levels.

[0022] As used herein, all concentrations and ratios are on a weight basis unless otherwise specified. All temperatures herein are in degrees Celsius (°C) unless otherwise indicated. All conditions herein are at 20°C and under the atmospheric pressure, unless otherwise specifically stated. All polymer molecular weights are determined by weight average number molecular weight unless otherwise specifically noted.

[0023] As mentioned hereinabove, flowability of highly concentrated anionic detergent granules (i.e., those with anionic surfactant concentrations as high as from about 40% to about 90%, preferably from about 50% to about 80%, by total weight of the detergent granules) is poor, due to worsened physical strength and stickier surface of such detergent granules in comparison with detergent granules of lower anionic surfactant concentrations. The poor flowability in turn leads to challenges in bulk-handling of such highly concentrated anionic detergent granules during the manufacturing process.

[0024] The present invention has discovered that by adding a non-quaternized alkoxylated polyethyleneimine (PEI) into such highly concentrated anionic detergent granules and then forming a silica coating layer thereover can significantly improve the flowability of such detergent granules, especially when such detergent granules contain high concentrations of alkylalkoxylated sulfate (AAS) surfactant(s).

[0025] Without being bound by any theories, inventors of the present invention believe that the alkoxylated PEI functions as a surfactant structurant to increase the particle strength of the detergent granules, while the silica coating layer functions to reduce the surface stickiness of the detergent granules. In combination, the alkoxylated PEI and the silica coating layer can significantly improve the flowability of the detergent granule, while flowability improvement achieved by either adding the alkoxylated PEI alone or forming the silica coating layer alone is much less significant.

CORE

[0026] The core of the detergent granule of the present invention may be characterized by a median particle size ranging from about 100 μm (microns) to about 900 μm (microns), preferably from about 300 μm (microns) to about 800 μm (microns), and more preferably from about 400 μm (microns) to about 700 μm (microns).

[0027] Anionic Surfactant(s): First, the core of the highly concentrated anionic detergent granule of the present invention contains one or more anionic surfactants, which are present in the amount ranging from about 40% to about 90%, preferably from about 50% to about 80%, by weight of such detergent granule.

[0028] Any suitable anionic surfactants can be used for the practice of the present invention. Preferably, the one or more anionic surfactants are selected from the group consisting of: (1) a C_{10} - C_{20} linear or branched alkylalkoxylated sulfate (AAS) surfactant; (2) a C_6 - C_{20} linear or branched unalkoxylated alkyl sulfate (AS) surfactant; (3) a C_{10} - C_{20} linear alkyl benzene sulphonate (LAS) surfactant; and (4) combinations thereof.

[0029] In a preferred embodiment of the present invention, the core of the highly concentrated anionic detergent granule of the present invention contains a C_{10} - C_{20} linear or branched alkylalkoxylated sulfate (AAS) surfactant having a weight average degree of alkoxylation ranging from about 0.1 to about 10, preferably from about 0.1 to about 5. A particularly preferred AAS surfactant for the practice of the present invention is a C_{12} - C_{18} linear alkylethoxylated sulfate (AES) having a weight average degree of ethoxylation of from about 0.5 to about 3.0, preferably from about 0.5 to about 2, more preferably from about 0.5 to about 1. More preferably, the AAS surfactant is a C_{12} - C_{14} linear alkylethoxylated sulfate (AES) surfactant having a weight average degree of ethoxylation of from about 0.5 to about 1.

[0030] Such AAS surfactant may be present in the core in an amount ranging from about 20% to about 90%, preferably from about 30% to about 90%, more preferably from about 40% to about 80%, most preferably from about 50% to about 70%, by total weight of said core. In a particularly preferred, but not necessary, embodiment of the present invention, the core comprises only one surfactant, which is the AAS surfactant. In another preferred embodiment of the present invention, the core comprises two or more surfactants, but the AAS surfactant is present as the main surfactant in such core, while one or more other surfactants (anionic, nonionic, amphoteric, and/or cationic) are present as co-surfactants.

[0031] The core of the highly concentrated anionic detergent granule of the present invention may contain a C_{10} - C_{20} linear alkyl benzene sulphonate (LAS) surfactant as the anionic surfactant, either alone or in combination with the above-mentioned AAS.

[0032] LAS surfactants are well known in the art and can be readily obtained by sulfonating commercially available linear alkylbenzenes. Exemplary C_{10} - C_{20} linear alkylbenzene sulfonates that can be used in the present invention include alkali metal, alkaline earth metal or ammonium salts of C_{10} - C_{20} linear alkylbenzene sulfonic acids, and preferably the sodium, potassium, magnesium and/or ammonium salts of C_{11} - C_{18} or C_{11} - C_{14} linear alkylbenzene sulfonic acids. More preferred are the sodium or potassium salts of C_{12} linear alkylbenzene sulfonic acids, and most preferred is the sodium salt of C_{12} linear alkylbenzene sulfonic acid, i.e., sodium dodecylbenzene sulfonate. If present, the amount of LAS in the core may range from about 5% to about 90%, preferably from about 10% to about 70%, and more preferably from about 15% to about 45%, by total weight of the core.

[0033] In a particularly preferred, but not necessary, embodiment of the present invention, the core of the highly concentrated anionic detergent granule of the present invention contains both the AAS surfactant and the LAS surfactant, while the weight ratio of AAS to LAS ranges from about 1:3 to about 10:1, preferably from about 1:2 to about 8:1, more preferably about 1:1 to about 5:1, most preferably from about 2:1 to about 4:1.

[0034] The core of the highly concentrated anionic detergent granule of the present invention may contain a C_{10} - C_{20} linear or branched unalkoxylated alkyl sulfate (AS) surfactant as the anionic surfactant, either alone or in combination with the above-mentioned AAS and/or LAS. The amount of AS in the core may range from about 50% to about 90%, preferable from about 60 to about 90%, and more preferably from about 65% to about 85% by total weight of the core.

[0035] The core may contain additional anionic surfactants (in addition to AAS, LAS and/or AS), such as C_{10} - C_{20} linear or branched alkyl sulphonates, C_{10} - C_{20} linear or branched alkyl phosphates, C_{10} - C_{20} linear or branched alkyl phosphonates, C_{10} - C_{20} linear or branched alkyl carboxylates, and salts and mixtures thereof.

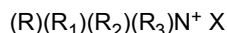
[0036] Other Surfactant(s): The core of the highly concentrated anionic detergent granule of the present invention may further contain, in addition to the above-mentioned anionic surfactants, one or more surfactants selected from the group consisting of nonionic surfactants, cationic surfactants, amphoteric surfactants, zwitterionic surfactant, and combinations thereof.

[0037] Suitable nonionic surfactants include alkoxyated fatty alcohols. The nonionic surfactant may be selected from ethoxylated alcohols and ethoxylated alkyl phenols of the formula $\text{R}(\text{OC}_2\text{H}_4)_n\text{OH}$, wherein R is selected from the group consisting of aliphatic hydrocarbon radicals containing from about 8 to about 15 carbon atoms and alkyl phenyl radicals in which the alkyl groups contain from about 8 to about 12 carbon atoms, and the average value of n is from about 5 to about 15. Non-limiting examples of nonionic surfactants useful herein include: C_8 - C_{18} alkyl ethoxylates, such as, NE-ODOL[®] nonionic surfactants from Shell; C_6 - C_{12} alkyl phenol alkoxyates where the alkoxyate units may be 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; C₁₄-C₂₂ mid-chain branched alcohols, BA; C₁₄-C₂₂ mid-chain branched alkyl alkoxylates, BAE_x, wherein x is from 1 to 30; alkylpolysaccharides; specifically alkylpolyglycosides; polyhydroxy fatty acid amides; and ether capped poly(oxyalkylated) alcohol surfactants. Suitable nonionic deterative surfactants also include alkyl polyglucoside and alkyl alkoxylated alcohol. Suitable nonionic surfactants also

[0038] Non-limiting examples of cationic surfactants include: the quaternary ammonium surfactants, which can have up to 26 carbon atoms include: alkoxylate quaternary ammonium (AQA) surfactants; dimethyl hydroxyethyl quaternary ammonium; dimethyl hydroxyethyl lauryl ammonium chloride; polyamine cationic surfactants; cationic ester surfactants; and amino surfactants, e.g., amido propyldimethyl amine (APA). Suitable cationic deterative surfactants also include alkyl pyridinium compounds, alkyl quaternary ammonium compounds, alkyl quaternary phosphonium compounds, alkyl ternary sulphonium compounds, and mixtures thereof.

[0039] Suitable 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, suitable anions include: halides, for example chloride; sulphate; and sulphonate. Suitable cationic deterative surfactants are mono-C₆₋₁₈ alkyl mono-hydroxyethyl di-methyl quaternary ammonium chlorides. Highly suitable cationic deterative surfactants are mono-C₈₋₁₀ alkyl mono-hydroxyethyl di-methyl quaternary ammonium chloride, mono-C₁₀₋₁₂ alkyl mono-hydroxyethyl di-methyl quaternary ammonium chloride and mono-C₁₀ alkyl mono-hydroxyethyl di-methyl quaternary ammonium chloride.

[0040] Suitable examples of zwitterionic surfactants include: derivatives of secondary and tertiary amines, including derivatives of heterocyclic secondary and tertiary amines; derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds; betaines, including alkyl dimethyl betaine, cocodimethyl amidopropyl betaine, and sulfo and hydroxy betaines; C₈ to C₁₈ (preferably from C₁₂ to C₁₈) amine oxides; N-alkyl-N,N-dimethylamino-1-propane sulfonate, where the alkyl group can be C₈ to C₁₈.

[0041] Suitable amphoteric surfactants include aliphatic derivatives of secondary or tertiary amines, or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic radical may be straight or branched-chain and where one of the aliphatic substituents contains at least about 8 carbon atoms, or from about 8 to about 18 carbon atoms, and at least one of the aliphatic substituents contains an anionic water-solubilizing group, e.g. carboxy, sulfonate, sulfate. Suitable amphoteric surfactants also include sarcosinates, glycinate, taurinate, and mixtures thereof.

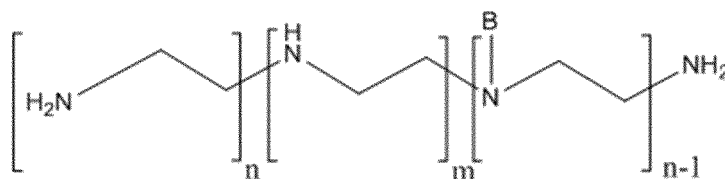
[0042] Non-quaternized Alkoxylated Polyethyleneimine: The core of the highly concentrated anionic detergent granule of the present invention contains, in addition to the anionic surfactants as described hereinabove, a non-quaternized alkoxylated polyethyleneimine having a polyalkyleneimine core with one or more alkoxy side chains bonded to at least one nitrogen atom in the polyalkyleneimine core, which may be present in the amount ranging from about 0.5% to about 10%, preferably from about 1% to about 5%, by total weight of the detergent granule.

[0043] Typically, the non-quaternized alkoxylated polyalkyleneimine is uncharged. The alkoxylated polyethyleneimine is typically non-quaternized at the pH of the concentrated surfactant composition. The non-quaternized alkoxylated polyethyleneimine may be linear, branched, or combinations thereof, preferably branched.

[0044] The non-quaternized alkoxylated polyalkyleneimine has a polyalkyleneimine (PEI) core with one or more alkoxy side chains bonded to at least one nitrogen atom in the polyalkyleneimine core.

[0045] Typically, the non-quaternized alkoxylated polyethyleneimine comprises a polyalkyleneimine backbone. The polyalkyleneimine may comprise C₂ alkyl groups, C₃ alkyl groups, or mixtures thereof, preferably C₂ alkyl groups. The non-quaternized alkoxylated polyethyleneimine polymer may have a polyethyleneimine ("PEI") backbone. The PEI backbone may have an average number-average molecular weight of from about 400 to about 1000, or from about 500 to about 750, or from about 550 to about 650, or about 600 Daltons, as determined prior to ethoxylation.

[0046] The PEI backbone of the polymers described herein, prior to alkoxylation, may have the general empirical formula:



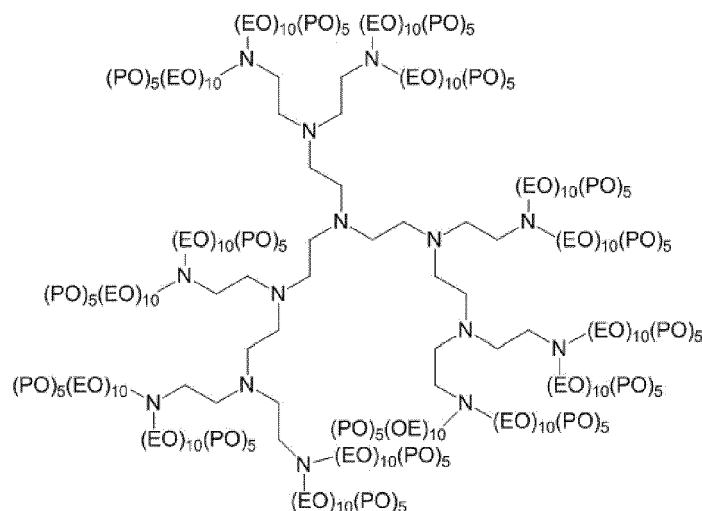
where B represents a continuation of this structure by branching. In some aspects, n+m is equal to or greater than 8, or 10, or 12, or 14, or 18, or 22.

[0047] The non-quaternized alkoxyated polyethyleneimine typically comprises alkoxyated nitrogen groups. The non-quaternized alkoxyated polyethyleneimine may independently comprise, on average per alkoxyated nitrogen, up to about 50, or up to about 40, or up to about 35, or up to about 30, or up to about 25, or up to about 20, alkoxyate groups. The non-quaternized alkoxyated polyethyleneimine may independently comprise, on average per alkoxyated nitrogen, at least about 5, or at least about 10, or at least about 15, or at least about 20, alkoxyate groups.

[0048] The alkoxyate groups may be ethoxylate (EO) groups, propoxylate (PO) groups, or combinations thereof, but are preferably ethoxylate (EO) groups. For example, the non-quaternized alkoxyated polyethyleneimine may comprise on average per alkoxyated nitrogen, about 1-50 ethoxylate (EO) groups and about 0-50 propoxylate (PO) groups. The non-quaternized alkoxyated polyethyleneimine may comprise on average per alkoxyated nitrogen, about 1-50 ethoxylate (EO) groups and is free of propoxylate (PO) groups. The non-quaternized alkoxyated polyethyleneimine may comprise on average per alkoxyated nitrogen, about 10-30 ethoxylate (EO) groups, preferably about 15-25 ethoxylate (EO) groups.

[0049] Suitable non-quaternized alkoxyated polyethyleneimine may include propoxylated polyalkylenimine (e.g., PEI) polymers. The propoxylated polyalkylenimine (e.g., PEI) polymers may also be ethoxylated. The propoxylated polyalkylenimine (e.g., PEI) polymers may have inner polyethylene oxide blocks and outer polypropylene oxide blocks, the degree of ethoxylation and the degree of propoxylation not going above or below specific limiting values. The ratio of polyethylene blocks to polypropylene blocks (n/p) may be from about 0.6, or from about 0.8, or from about 1, to a maximum of about 10, or a maximum of about 5, or a maximum of about 3. The n/p ratio may be about 2. The propoxylated polyalkylenimines may have PEI backbones having weight average molecular weights (as determined prior to alkoxylation) of from about 200 g/mol to about 1200 g/mol, or from about 400 g/mol to about 800 g/mol, or about 600 g/mol. The molecular weight of the propoxylated polyalkylenimines may be from about 8,000 to about 20,000 g/mol, or from about 10,000 to about 15,000 g/mol, or about 12,000 g/mol.

[0050] Suitable propoxylated polyalkylenimine polymers may include compounds of the following structure:



where EOs are ethoxylate groups and POs are propoxylate groups. The compound shown above is a PEI where the molar ratio of EO:PO is about 10:5 (e.g., 2:1). Other similar, suitable compounds may include EO and PO groups present in a molar ratio of about 10:5 or about 24:16.

[0051] Suitable polyamines include low molecular weight, water soluble, and lightly alkoxyated ethoxylated/propoxylated polyalkyleneamine polymers. By "lightly alkoxyated," it is meant the polymers of this invention average from about 0.5 to about 20, or from 0.5 to about 10, alkoxyations per nitrogen. The polyamines may be "substantially noncharged," meaning that there are no more than about 2 positive charges for every about 40 nitrogens present in the backbone of the polyalkyleneamine polymer at pH 10, or at pH 7; it is recognized, however, that the charge density of the polymers may vary with pH.

[0052] Suitable alkoxyated polyalkyleneimines, such as PEI₆₀₀EO₂₀, are available from BASF (Ludwigshafen, Germany).

[0053] Ethylene oxide-propylene oxide-ethylene oxide (EO/PO/EO) triblock copolymer: The core of the highly concentrated anionic detergent granule of the present invention may further contain, in addition to the anionic surfactants and the PEI polymers mentioned hereinabove, an ethylene oxide-propylene oxide-ethylene oxide (EO/PO/EO) triblock copolymer, which preferably has an average propylene oxide chain length of between about 20 and about 70, preferably

between about 30 and about 60, more preferably between about 45 and about 55 propylene oxide units.

[0054] Preferably, the ethylene oxide-propylene oxide-ethylene oxide (EO/PO/EO) triblock copolymer has a weight average molecular weight of between about 1000 and about 10,000, preferably between about 1500 and about 5000 more preferably between about 2000 and about 4500, even more preferably between about 2500 and about 4000, most preferably between about 3500 and about 3800 Daltons.

[0055] Preferably, each ethylene oxide block or chain independently has an average chain length of between about 2 and about 90, preferably about 3 and about 50, more preferably between about 4 and about 20 ethylene oxide units.

[0056] Preferably, the copolymer comprises between about 10% and about 90%, preferably between about 15% and about 50%, most preferably between about 15% and about 25% by weight of the copolymer of the combined ethylene-oxide blocks. Most preferably the total ethylene oxide content is equally split over the two ethylene oxide blocks. Equally split herein means each ethylene oxide block comprising on average between about 40% and about 60% preferably between about 45% and about 55%, even more preferably between about 48% and about 52%, most preferably about 50% of the total number of ethylene oxide units, the % of both ethylene oxide blocks adding up to 100%.

[0057] Most preferably the copolymer has a weight average molecular weight between about 3500 and about 3800 Daltons, a propylene oxide content between about 45 and about 55 propylene oxide units, and an ethylene oxide content of between about 4 and about 20 ethylene oxide units per ethylene oxide block.

[0058] Suitable ethylene oxide - propylene oxide - ethylene oxide triblock copolymers are commercially available under the Pluronic PE series from the BASF company, or under the Tergitol L series from the Dow Chemical Company. A particularly suitable material is Pluronic PE 9200.

[0059] Solid Carrier: Further, the core of the highly concentrated anionic detergent granule of the present invention may contain a solid carrier selected from the group consisting of: zeolite, silica, carboxymethyl cellulose, modified starch, and combinations thereof. Preferably, such solid carrier is present in an amount ranging from about 5% to about 50%, preferably from about 15% to about 45%, more preferably from about 20% to about 30%, by total weight of the detergent granule.

[0060] In a particularly preferred embodiment of the present invention, the solid carrier is silica, and more preferably hydrophilic silica. Silica has both internal and external surface area, which allows for easy absorption of liquids and has a large liquid loading capacity. Hydrophilic silica is especially effective at adsorbing water. Any silica particles with suitable particle sizes can be employed for practice of the present invention. Specifically, the silica particles have a dry particle size distribution D_{w50} ranging from about 0.1 μm to about 100 μm , preferably from about 1 μm to about 50 μm , more preferably from about 2 μm to about 40 μm , and most preferably from 4 μm to about 20 μm .

[0061] Preferably but not necessarily, the silica particles are composed of hydrophilic silica that can be hydrated upon contact with the washing liquor to expand volumetrically. Without being bound by any theory, it is believed that the volumetric expansion of hydrophilic silica helps to up disintegration of the detergent granule and leads to faster dispersion and dissolution of the anionic surfactants into the washing liquor. Therefore, hydrophilic silica, and preferably precipitated hydrophilic silica, is incorporated into the core of the detergent granule of the present invention together with anionic surfactants therein to provide higher surfactant activity and faster dispersion or dissolution benefits. A particularly preferred hydrophilic precipitated silica material for practice of the present invention is commercially available from Evonik Corporation under the tradename Sipernat®340.

[0062] The silica is preferably present in the core of the detergent granules in an amount ranging from about 10 wt% to about 50 wt%, more preferably from about 15 wt% to about 45 wt%, and most preferably from about 20 wt% to about 30 wt%, by total weight of the detergent granules.

[0063] Water-Soluble Inorganic Salt: Further, the core of the highly concentrated anionic detergent granule of the present invention may contain a water-soluble inorganic salt selected from the group consisting of sodium sulfate, potassium sulfate, sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate, and combinations thereof. Particularly preferred examples of water-soluble inorganic salts for the practice of the present invention include sodium sulfate and sodium carbonate, while sodium sulfate is most preferred. Such water-soluble inorganic salt may be present in an amount ranging from about 1% to about 20%, preferably from about 2% to about 15%, more preferably from about 3% to about 10%, by total weight of the detergent granule.

[0064] Optionally, particle size of the salt(s) may be reduced by a milling, grinding or a comminuting step with any apparatus known in the art for milling, grinding or comminuting of granular or particulate compositions.

[0065] Other Cleaning Actives: In addition to the above-mentioned ingredients, the core may, but do not need to, further comprise one or more other cleaning actives, such as chelants, polymers, enzymes, bleaching agents, and the like. In a particularly preferred embodiment of the present invention, the core of the highly concentrated anionic detergent granule of the present invention is substantially free of such other cleaning actives.

COATING LAYER

[0066] A coating layer containing silica is formed over the core of the detergent granule of the present invention. Such

coating layer may cover only a portion of the core, or the entire outer surface of the core. The coating layer is preferably a continuous layer, but it can also be discontinuous and covering discrete regions of the outer surface of the core. Such a coating layer of silica may be present in an amount ranging from about 1% to about 10%, preferably from about 2% to about 5%, by total weight of the detergent granule.

[0067] The silica used for forming the coating layer may be the same or different from the silica used as the solid carrier in the core. Preferably, the silica in the coating layer is the same as that used in the core. More preferably, the silica in the coating layer is hydrophilic silica, especially precipitated hydrophilic silica. A particularly preferred hydrophilic precipitated silica material for practice of the present invention is commercially available from Evonik Corporation under the tradename Sipemat®340.

DETERGENT GRANULE

[0068] The detergent granule of the present invention may have a particle size distribution such that the D50 is from greater than about 150 micrometers to less than about 1700 micrometers. The detergent granule may have a particle size distribution such that the D50 is from greater than about 212 micrometers to less than about 1180 micrometers. The detergent granule may have a particle size distribution such that the D50 is from greater than about 300 micrometers to less than about 850 micrometers. The detergent granule may have a particle size distribution such that the D50 is from greater than about 350 micrometers to less than about 700 micrometers. The detergent granule may have a particle size distribution such that the D20 is greater than about 150 micrometers and the D80 is less than about 1400 micrometers.

The detergent granule may have a particle size distribution such that the D20 is greater than about 200 micrometers and the D80 is less than about 1180 micrometers. The detergent granule may have a particle size distribution such that the D20 is greater than about 250 micrometers and the D80 is less than about 1000 micrometers. The detergent granule may have a particle size distribution such that the D10 is greater than about 150 micrometers and the D90 is less than about 1400 micrometers. The detergent granule may have a particle size distribution such that the D10 is greater than about 200 micrometers and the D90 is less than about 1180 micrometers. The detergent granule may have a particle size distribution such that the D10 is greater than about 250 micrometers and the D90 is less than about 1000 micrometers.

[0069] In another context, the detergent granule may be used in a bead-like detergent or derivative thereof. The detergent granule may have a particle size distribution such that the D50 is from greater than about 1mm to less than about 4.75mm. The detergent granule may have a particle size distribution such that the D50 is from greater than about 1.7mm to less than about 3.5mm. The detergent granule may have a particle size distribution such that the D20 is greater than about 1mm and the D80 is less than about 4.75mm. The detergent granule may have a particle size distribution such that the D20 is greater than about 1.7mm and the D80 is less than about 3.5mm. The detergent granule may have a particle size distribution such that the D10 is greater than about 1mm and the D90 is less than about 4.75mm. The detergent granule may have a particle size distribution such that the D10 is greater than about 1.7mm and the D90 is less than about 3.5mm.

[0070] The bulk density of such detergent granule may range from about 300g/L to about 900 g/L, preferably from about 400g/L to about 800g/L, more preferably from about 450g/L to about 550g/L.

[0071] The detergent granule of the present invention preferably has a total moisture content of no more than about 5%, preferably no more than about 3%, more preferably no more than about 2.5%, by total weight of such detergent granule.

GRANULAR DETERGENT COMPOSITION

[0072] The above-described detergent granules are particularly useful for forming high active granular detergent compositions of improved water hardness resistance, fast surfactant release and better dissolution or dispersion. Such detergent granules may be provided in a granular detergent composition in an amount ranging from 1% to 99%, preferably from about 2% to about 80%, and more preferably from about 5% to about 50% by total weight of the granular detergent composition.

[0073] The granular detergent composition may comprise one or more additional surfactants that are added directly therein, i.e., independent of the detergent granules as described hereinabove. The additional surfactants can be same as those already included in the detergent granules, or they can be different. The same types of anionic surfactants and other surfactants as described hereinabove are also suitable for directly addition into the granular detergent composition.

[0074] The granular detergent compositions of the present invention may further comprise a water-swellaable cellulose derivative. Suitable examples of water-swellaable cellulose derivatives are selected from the group consisting of substituted or unsubstituted alkyl celluloses and salts thereof, such as ethylcellulose, hydroxyethyl cellulose, hydroxypropyl methyl cellulose, methyl cellulose, carboxyl methyl cellulose (CMC), cross-linked CMC, modified CMC, and mixtures thereof. Preferably, such cellulose derivative materials can rapidly swells up within about 10 minutes, preferably within about 5 minutes, more preferably within about 2 minutes, even more preferably within about 1 minute, and most preferably within

about 10 seconds, after contact with water. The water-swellaable cellulose derivatives can be incorporated into the structured particles of the present invention together with the hydrophilic silica, or they can be incorporated into the granular detergent compositions independent of the structured particles, in an amount ranging from about 0.1% to about 5% and preferably from about 0.5% to about 3%. Such cellulose derivatives may further enhance the mechanical cleaning benefit of the granular detergent compositions of the present invention.

[0075] The granular detergent compositions may optionally include one or more other detergent adjunct materials for assisting or enhancing cleaning performance, treatment of the substrate to be cleaned, or to modify the aesthetics of the detergent composition. Illustrative examples of such detergent adjunct materials include: (1) inorganic and/or organic builders, such as carbonates (including bicarbonates and sesquicarbonates), sulphates, phosphates (exemplified by the tripolyphosphates, pyrophosphates, and glassy polymeric meta-phosphates), phosphonates, phytic acid, silicates, zeolite, citrates, polycarboxylates and salts thereof (such as mellitic acid, succinic acid, oxydisuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof), ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1,3,5-trihydroxy benzene-2,4,6-trisulphonic acid, 3,3-dicarboxy-4-oxa-1,6-hexanedioates, polyacetic acids (such as ethylenediamine tetraacetic acid and nitrilotriacetic acid) and salts thereof, fatty acids (such as C₁₂-C₁₈ monocarboxylic acids); (2) chelating agents, such as iron and/or manganese-chelating agents selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures therein; (3) clay soil removal/anti-redeposition agents, such as water-soluble ethoxylated amines (particularly ethoxylated tetraethylenepentamine); (4) polymeric dispersing agents, such as polymeric polycarboxylates and polyethylene glycols, acrylic/maleic-based copolymers and water-soluble salts thereof, hydroxypropylacrylate, maleic/acrylic/vinyl alcohol terpolymers, polyethylene glycol (PEG), polyaspartates and polyglutamates; (5) optical brighteners, which include but are not limited to derivatives of stilbene, pyrazoline, coumarin, carboxylic acid, methinecyanines, dibenzothiphen-5,5-dioxide, azoles, 5- and 6-membered-ring heterocycles, and the like; (6) suds suppressors, such as monocarboxylic fatty acids and soluble salts thereof, high molecular weight hydrocarbons (e.g., paraffins, haloparaffins, fatty acid esters, fatty acid esters of monovalent alcohols, aliphatic C₁₈-C₄₀ ketones, etc.), N-alkylated amino triazines, propylene oxide, monostearyl phosphates, silicones or derivatives thereof, secondary alcohols (e.g., 2-alkyl alkanols) and mixtures of such alcohols with silicone oils; (7) suds boosters, such as C₁₀-C₁₆ alkanolamides, C₁₀-C₁₄ monoethanol and diethanol amides, high sudsing surfactants (e.g., amine oxides, betaines and sultaines), and soluble magnesium salts (e.g., MgCl₂, MgSO₄, and the like); (8) fabric softeners, such as smectite clays, amine softeners and cationic softeners; (9) dye transfer inhibiting agents, such as polyvinyl pyrrolidone polymers, polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, manganese phthalocyanine, peroxidases, and mixtures thereof; (10) enzymes, such as proteases, amylases, lipases, cellulases, and peroxidases, and mixtures thereof; (11) enzyme stabilizers, which include water-soluble sources of calcium and/or magnesium ions, boric acid or borates (such as boric oxide, borax and other alkali metal borates); (12) bleaching agents, such as percarbonates (e.g., sodium carbonate peroxyhydrate, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, and sodium peroxide), persulfates, perborates, magnesium monoperoxyphthalate hexahydrate, the magnesium salt of metachloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid, 6-nonylamino-6-oxoperoxyacaproic acid, and photoactivated bleaching agents (e.g., sulfonated zinc and/or aluminum phthalocyanines); (13) bleach activators, such as nonanoyloxybenzene sulfonate (NOBS), tetraacetyl ethylene diamine (TAED), amido-derived bleach activators including (6-octanamidocaproyl)oxybenzenesulfonate, (6-nonanamidocaproyl)oxybenzenesulfonate, (6-decanamidocaproyl)oxybenzenesulfonate, and mixtures thereof, benzoxazin-type activators, acyl lactam activators (especially acyl caprolactams and acyl valerolactams); and (9) any other known detergent adjunct ingredients, including but not limited to carriers, hydrotropes, processing aids, dyes or pigments, and solid fillers.

PROCESS FOR MAKING DETERGENT GRANULES

[0076] In an embodiment of the present invention, the detergent granule is formed in at least three steps, including a first step of forming an aqueous paste comprising the one or more anionic surfactants, the non-quaternized alkoxyated polyethyleneimine, and water; a second step of mixing the aqueous paste from the first step with a solid carrier to form a core particle; and a third step of coating silica over said core particle to form the coating layer.

[0077] Concentrated surfactant pastes are intermediate compositions that may be combined with other ingredients to form the detergent granule of the current invention. Concentrated surfactant compositions may comprise, may consist essentially of, or may consist of the following components: a surfactant system that may include an AAS surfactant and/or a LAS surfactant; an alkoxyated amine, preferably an alkoxyated polyamine; an organic solvent system; and water.

[0078] Preferably, the concentrated surfactant composition may comprise: from about 70% to about 90%, by weight of the composition, of a surfactant system, where the surfactant system comprises from about 50%, or from about 60%, or from about 70%, or from about 80%, to about 100%, of AAS surfactant; from about 0.1% to about 25%, by weight of

the composition, of an alkoxyated polyethyleneimine (PEI); less than about 5%, by weight of the composition, of an organic solvent system; and water.

Process for Making the Granular Detergent Compositions Comprising the Detergent Granules

[0079] The granular detergent composition, which is provided in a finished product form, can be made by mixing the detergent granules of the present invention with a plurality of other particles containing the above-described additional surfactants, cellulose derivatives, and detergent adjunct materials. Such other particles can be provided as spray-dried particles, agglomerated particles, and extruded particles. Further, the additional surfactants, cellulose derivatives, and detergent adjunct materials can also be incorporated into the granular detergent composition in liquid form through a spray-on process.

Process for Using the Granular Detergent Compositions

[0080] The granular detergent compositions of the present invention can be used for either machine washing or hand washing of fabrics. It is particularly suitable for use in a hand-washing context. For hand-washing, the laundry detergent is typically diluted by a factor of from about 1:100 to about 1:1000, or about 1:200 to about 1:500 by weight, by placing the laundry detergent in a container along with wash water to form a laundry liquor. The wash water used to form the laundry liquor is typically whatever water is easily available, such as tap water, river water, well water, etc. The temperature of the wash water may range from about 0°C to about 40°C, preferably from about 5°C to about 30°C, more preferably from about 5°C to about 25°C, and most preferably from about 10°C to about 20°C, although higher temperatures may be used for soaking and/or pretreating.

[0081] The laundry detergent and wash water is usually agitated to evenly disperse and/or either partially or completely dissolve the detergent and thereby form a laundry liquor. Such agitation forms suds, typically voluminous and creamy suds. The dirty laundry is added to the laundry liquor and optionally soaked for a period of time. Such soaking in the laundry liquor may be overnight, or for from about 1 minute to about 12 hours, or from about 5 minutes to about 6 hours, or from about 10 minutes to about 2 hours. In a variation herein, the laundry is added to the container either before or after the wash water, and then the laundry detergent is added to the container, either before or after the wash water. The method herein optionally includes a pre-treating step where the user pre-treats the laundry with the laundry detergent to form pre-treated laundry. In such a pre-treating step, the laundry detergent may be added directly to the laundry to form the pre-treated laundry, which may then be optionally scrubbed, for example, with a brush, rubbed against a surface, or against itself before being added to the wash water and/or the laundry liquor. Where the pre-treated laundry is added to water, then the diluting step may occur as the laundry detergent from the pre-treated laundry mixes with the wash water to form the laundry liquor.

[0082] The laundry is then hand-washed by the user who may or may not use one or more handheld washing devices, such as washboards, brushes, or rods. The actual hand-washing duration may range from about 10 seconds to about 30 minutes, preferably from about 30 seconds to about 20 minutes, more preferably from about 1 minute to about 15 minutes, and most preferably from about 2 minutes to about 10 minutes. Once the laundry is hand-washed, then the laundry may be wrung out and put aside while the laundry liquor is either used for additional laundry, poured out, etc. The rinse water is then added to form a rinse bath, and then it is common practice to agitate the laundry to remove the surfactant residue. The laundry may be soaked in the rinse water and then wrung out and put aside. The number of rinses when using the liquid laundry detergent herein is typically from about 1 to about 3, or from about 1 to about 2. In a particularly preferred embodiment of the present invention, the rinse is carried out in a single rinse step or cycle.

TEST METHODS

[0083] The following techniques must be used to determine the properties of the detergent granules and detergent compositions of the invention in order that the invention described and claimed herein may be fully understood.

Test 1: Moisture Content Measurement

[0084] Two (2) grams of a sample detergent granule is tested in the Mettler Toledo HR73 Halogen moisture analyzer at 120°C for 30 minutes. The percentage (%) of lost mass at the end of the measurement is recorded as the moisture content of the sample detergent granule.

Test 2: Particle Size Distribution Test

[0085] The particle size distribution of the detergent granule is determined by using ASTM D 502 - 89, "Standard Test

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Method for Particle Size of Soaps and Other Detergents", approved May 26, 1989, with a further specification for sieve sizes and sieve time used in the analysis. Following section 7, "Procedure using machine-sieving method," a nest of clean dry sieves: 1400 micrometer, 1180 micrometer, 850 micrometer, 600 micrometer, 425 micrometer, 250 micrometer, 150 micrometer, is required to cover the range of particle sizes referenced herein. The prescribed machine-sieving method is used with the above sieve nest. A suitable sieve-shaking machine can be obtained from W.S. Tyler Company, Ohio, U.S.A. The sieve-shaking test sample is approximately 100 grams and is shaken for 5 minutes.

[0086] The data are plotted on a semi-log plot with the micrometer size opening of each sieve plotted against the logarithmic abscissa and the cumulative mass percent (Q_3) plotted against the linear ordinate. An example of the above data representation is given in ISO 9276-1:1998, "Representation of results of particle size analysis - Part 1: Graphical Representation", Figure A.4. A characteristic particle size (D_x), for the purpose of this invention, is defined as the abscissa value at the point where the cumulative mass percent is equal to x percent, and is calculated by a straight-line interpolation between the data points directly above (a) and below (b) the $x\%$ value using the following equation:

$$D_x = 10^{\left[\text{Log}(D_a) - \frac{(\text{Log}(D_a) - \text{Log}(D_b)) \cdot (Q_a - x\%)}{(Q_a - Q_b)} \right]}$$

where Log is the base 10 logarithm, Q_a and Q_b are the cumulative mass percentile values of the measured data immediately above and below the x^{th} percentile, respectively; and D_a and D_b are the micrometer sieve size values corresponding to these data.

[0087] For example, for the following exemplary data set:

sieve size (micrometer)	mass% of sample from each sieve (g)	cumulative mass% finer (CMPF)
1400	0%	99.9%
1180	13.6%	86.3%
850	17.7%	68.6%
600	19.9%	48.7%
425	21.1%	27.6%
250	24.1%	3.5%
150	3.1%	0.4%
Pan	0.4%	0.0%

[0088] The corresponding D_{50} ($x = 50\%$) can then be calculated use the equation above. Specifically, the micrometer screen size where CMPF is immediately above 50% (D_a) is 850 micrometers, while the screen below (D_b) is 600 micrometers. The cumulative mass immediately above 50% (Q_a) is 68.6%, below (Q_b) is 48.7%. Therefore, $D_{50} = 10^{\left[\text{Log}(850) - \frac{(\text{Log}(850) - \text{Log}(600)) \cdot (68.6\% - 50\%)}{(68.6\% - 48.7\%)} \right]} = 614$ micrometer.

EXAMPLES

Example 1: Exemplary Detergent Granule Formulations:

[0089]

TABLE I

Ingredients (wt%)		A	B	C	D
Core	AES (with EO1)	45	50	20	45
	LAS	25	10	40	15
	Silica*	22.7	24.8	24.8	24.8
	PEI ₆₀₀ EO ₂₀	2	2	5	2
	Sodium Carbonate or Sodium sulfate	0	8.5	5.5	8.5
	Misc.**	2.8	2.2	2.2	2.2
	Water	2.5	2.5	2.5	2.5
Coating	Silica*	2	2	2	2
Total		100	100	100	100
*Sipernat@ 340					
**Including NaOH, salts, and solvents from surfactant raw material.					

Example 2: Comparative Tests Showing Flowability Improvement

[0090] Four sample detergent granules are provided, including: (1) a control sample ("Control") that contains neither the alkoxylated PEI polymer nor the silica coating layer; (2) a first comparative sample ("C1") that contains only the alkoxylated PEI polymer in the core, but without the silica coating layer; (3) a second comparative sample ("C2") that contains only the silica coating layer, but no alkoxylated PEI polymer in the core; and (4) an inventive samples ("S1") that contain both the alkoxylated PEI polymer in the core and the silica coating layer. The formulations of such sample detergent granules are listed as follows:

TABLE II

Ingredients (wt%)		Control	C1	C2	S1
Core	AE1S	45	45	45	45
	LAS	15	15	15	15
	Silica*	26	26	26	26
	PEI ₆₀₀ EO ₂₀	0	1.8	0	1.8
	Sodium sulfate	9.3	7.5	7.3	5.5
	Misc.**	2.2	2.2	2.2	2.2
	Water	2.5	2.5	2.5	2.5
Coating	Silica*	0	0	2	2
Total		100	100	100	100
*Sipernat@ 340					
** Including NaOH, salts, and solvents from surfactant raw material.					

[0091] The sample detergent granules as listed hereinabove can be made by a suitable binder-agglomeration process. The process can be batch or continuous. The particle size distribution is one of the key factors influencing particle flowability. Therefore, it is important to ensure that all sample detergent granules have the same or substantially similar particle size distributions, in order to minimize any potential impact of the particle size distribution variations on the flowability test results. The same or substantially similar particle size distribution for all sample detergent granules can be obtained by sieving the sample detergent granules with a nest of clean dry sieves using a sieve-shaking machine. The sieved samples from each sieve can then be combined to form a sample detergent granule characterized by a desired particle size distribution. For example, all sample detergent granules tested herein are all characterized by a D50 of approximately 614 micrometers, measured by Test 2 described hereinabove.

[0092] Before running the flowability test, each of the sample detergent granules is left in an open petri dish as a thin layer under the ambient condition (20-22°C and 35-40%RH) to allow them to absorb moisture from the ambience for about 1 day. The samples need to reach an eRH of 30-35% before running the flowability test.

[0093] The flowability (ff_c) of each sample detergent granule is the ratio of σ_1 (consolidation stress) to σ_c (unconfined yield strength), which is used to characterize flowability numerically: the larger ff_c means the better a bulk solid flows. The flowability (ff_c) data is generated from a Schulze Ring Shear Tester RST-XS (as shown in FIG. 1), while the detailed test procedure of the ring shear tester is described in detail in ASTM standard D-6773.

[0094] The specific operating condition of the Schulze Ring Shear Tester RST-XS are described hereinafter. To run a flow-ability test, firstly fill sufficient pre-conditioned detergent granules into the shear cell and form a flat powder bed by scraping off the excess material with a spatula. The mass of the filled bottom ring is then weighed and recorded. Set the filled bottom ring on the ring shear tester and place the lid concentrically to the bottom ring on the bulk solid specimen. For preshear the bottom ring is rotated clockwise (seen from the top), whereby the lid is prevented from rotation by the tie rods. The consolidation stress at pre-shear is set as 16000Pa, and five different other consolidation stresses (3200Pa, 4800Pa, 6400Pa, 8000Pa and 9600Pa) are also applied during the same test. The minimum shear stress required to shear the bulk sample (shear to failure) at each consolidation stress is then measured to generate a yield locus (see Fig 4.10 in D. Schulze, Powder and Bulk Solid: Behavior, Characterization, Storage and Flow, Springer, 2008). The yield locus is then used to calculate the consolidation stress, σ_1 and the unconfined yield strength, σ_c ; and the ratio of σ_1 to σ_c is the flowability, ff_c . Following are the flowability test results of the sample detergent granules:

TABLE III

	Control	C1	C2	S1
	(No PEI; No Silica Coating)	(PEI only; No Silica Coating)	(No PEI; Silica Coating Only)	(PEI and Silica Coating)
Flowability (ff_c)	2.08	2.04	3.20	4.26
Δff_c	--	-0.04	1.12	2.18

[0095] The above flowability data shows that the combination of alkoxyated PEI polymer in the core and the silica coating thereover in the inventive sample detergent granule S1 surprisingly and unexpected improves the flowability of such detergent granule, significantly above the flowability improvement observed by either adding the alkoxyated PEI polymer alone or providing the silica coating layer alone.

Example 3: Comparative Tests Showing Improvement in Particle Yield Stress

[0096] The four (4) sample detergent granules of Example 2 (i.e., control, C1, C2 and S1) are also subjected to the following compressive force test:

A suitable mechanical testing machine (INSTRON 3369 with compaction platens and a punch and die set to measure compression up to at least 10 MPa pressure) is used. Put the bottom punch into the die. Add a sufficient sample of detergent granules (250-850 μ m) into the die, to form a tablet having a height to diameter ratio of from about 0.2 to about 0.5. Add the top punch gently until it rests on the powder. Put the die and punch between the platens of the mechanical testing machine. Move the top platen to less than about 1mm from the top of the punch. Execute a compressive test to a force that is equivalent to a pressure limit of at least 10 MPa. After compression, retract the platen, remove die and punch, eject the tablet, and measure the height and mass of the tablet.

[0097] After above procedure, the compaction curve recoded in the system can be used to calculate yield stress data following below procedure: The compaction curve onset calculation is done by taking tangent lines from particle rearrangement region to particle deformation region, positioned close to the transition in the curve, and solving for the intersection of the tangents. The first derivative of the compaction curve is used to position the tangent points at each side end of the slope transition. The apparent yield stress can be defined by this onset analysis. For detailed data analysis methodology, refer to "Analysis and application of powder compaction diagrams," P. Mort in A. Levy, H. Kalman (Eds.) Handbook of Conveying and Handling of Particulate Solids, Elsevier Science, 2001. Following are the apparent yield stress (MPa) of the sample detergent granules:

TABLE IV

	Control	C1	C2	S1
	(No PEI; No Silica Coating)	(PEI only; No Silica Coating)	(No PEI; Silica Coating Only)	(PEI and Silica Coating)
Yield stress (MPa)	0.032	0.118	0.071	0.173
Δ MPa	--	0.086	0.039	0.141

[0098] The above yield stress data shows that the combination of alkoxyated PEI polymer in the core and the silica coating thereover in the inventive sample detergent granule S1 surprisingly and unexpectedly improves the physical strength of such detergent granule, significantly above the improvement observed by either adding the alkoxyated PEI polymer alone or providing the silica coating layer alone. 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 cited herein, the meaning or definition assigned to that term in this document shall govern.

Claims

1. A detergent granule **characterized by** a total anionic surfactant content ranging from 40% to 90% by weight, said detergent granule comprising:
 - a core that comprises: (a) one or more anionic surfactants; and (b) a non-quaternized alkoxyated polyethyleneimine having a polyalkyleneimine core with one or more alkoxy side chains bonded to at least one nitrogen atom in the polyalkyleneimine core; and
 - a coating layer over the core, said coating layer comprising silica.
2. The detergent granule of claim 1, wherein said one or more anionic surfactants are selected from the group consisting of: (1) a C₁₀-C₂₀ linear or branched alkylalkoxyated sulfate (AAS) surfactant; (2) a C₆-C₂₀ linear or branched unalkoxyated alkyl sulfate (AS) surfactant; (3) a C₁₀-C₂₀ linear alkyl benzene sulphonate (LAS) surfactant; and (4) combinations thereof.
3. The detergent granule of claim 2, wherein said core comprises only one surfactant that is the C₁₀-C₂₀ linear or branched alkylalkoxyated sulfate (AAS) surfactant.
4. The detergent granule of claim 2, wherein said core comprises the C₁₀-C₂₀ linear or branched alkylalkoxyated sulfate (AAS) surfactant and the C₁₀-C₂₀ linear alkyl benzene sulphonate (LAS) surfactant, wherein the weight ratio of AAS to LAS ranges from 1:3 to 10:1, preferably from 1:2 to 8:1, more preferably 1:1 to 5:1, most preferably from 2:1 to 4:1.
5. The detergent granule according to any one of claims 2-4, wherein the AAS surfactant is a C₁₂-C₁₈ linear alkylethoxyated sulfate (AES) having a weight average degree of ethoxylation of from 0.5 to 3.0, preferably from 0.5 to 2, more preferably from 0.5 to 1.
6. The detergent granule according to any one of claims 1-5, wherein the non-quaternized alkoxyated polyethyleneimine has an empirical formula (I) of (PEI)_a-(EO)_b-R_i, wherein a is the average number-average molecular weight of the polyalkyleneimine core (MWPEI) of the alkoxyated polyalkyleneimine and is in the range of from about 100 to about 100,000 Daltons, wherein b is the weight average degree of ethoxylation in said one or more side chains of the alkoxyated polyalkyleneimine and is in the range of from about 5 to about 40, and wherein R_i is independently selected from the group consisting of hydrogen, C₁-C₄ alkyl, and combinations thereof.
7. The detergent granule according to any one of claims 1-5, wherein the non-quaternized alkoxyated polyethyleneimine has an empirical formula (II) of (PEI)_o-(EO)_m-(PO)_n-R₂ or (PEI)_o-(PO)_n-(EO)_m-R₂, wherein o is the average number-average molecular weight of the polyalkyleneimine core (MWPEI) of the alkoxyated polyalkyleneimine and

is in the range of from 100 to 100,000 Daltons, wherein m is the weight average degree of ethoxylation in said one or more side chains of the alkoxyated polyalkyleneimine which ranges from 10 to 50, wherein n is the weight average degree of propoxylation in said one or more side chains of the alkoxyated polyalkyleneimine which ranges from 1 to 50, and wherein R₂ is independently selected from the group consisting of hydrogen, C₁-C₄ alkyl, and combinations thereof.

8. The detergent granule according to any one of claims 1-7, wherein the non-quaternized alkoxyated polyethyleneimine is present in an amount ranging from 0.5% to 10%, preferably 1% to 5%, by total weight of said detergent granule.

9. The detergent granule according to any one of claims 1-8, wherein the core of said detergent granule further comprises a solid carrier selected from the group consisting of: zeolite, silica, carboxymethyl cellulose, modified starch, and combinations thereof; wherein preferably said solid carrier is silica; and wherein more preferably said solid carrier is present in an amount ranging from 5% to 50%, preferably from 15% to 45%, more preferably from 20% to 30%, by total weight of said detergent granule.

10. The detergent granule according to any one of claims 1-9, wherein the core of said detergent granule further comprises a water-soluble inorganic salt selected from the group consisting of sodium sulfate, potassium sulfate, sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate, and combinations thereof; and wherein preferably said water-soluble inorganic salt is present in an amount ranging from 1% to 20%, preferably from 2% to 15%, more preferably from 3% to 10%, by total weight of said detergent granule.

11. The detergent granule according to any one of claims 1-10, wherein the coating layer of silica is present in an amount ranging from 1% to 10%, preferably from 2% to 5%, by total weight of said detergent granule, and wherein preferably the silica is hydrophilic silica.

12. The detergent granule according to any one of claims 1-11, **characterized by** a total moisture content of no more than 5%, preferably no more than 3%, more preferably no more than 2.5%, by total weight of said detergent granule.

13. A granular detergent composition comprising from 1% to 99% of the detergent granule according to any one of claims 1-12.

14. A method of making the detergent granule according to any one of claims 1-12, comprising the steps of:

- (a) forming an aqueous paste comprising the one or more anionic surfactants, the non-quaternized alkoxyated polyethyleneimine, and water;
- (b) mixing the aqueous paste from step (a) with a solid carrier to form a core particle; and
- (c) coating silica over said core particle.

Patentansprüche

1. Waschmittelgranulat, **gekennzeichnet durch** einen Gesamtgehalt an Aniontensid im Bereich von 40 Gew.-% bis 90 Gew.-%, wobei das Waschmittelgranulat umfasst:

- einen Kern, der umfasst: (a) ein oder mehrere Aniontenside; und (b) ein nicht quaternisiertes alkoxyliertes Polyethylenimin mit einem Polyalkylenimin-Kern mit einer oder mehreren Alkoxyseitenketten, die an mindestens ein Stickstoffatom in dem Polyalkylenimin-Kern gebunden sind; und
- eine Beschichtungsschicht über dem Kern, wobei die Beschichtungsschicht Siliciumdioxid umfasst.

2. Waschmittelgranulat nach Anspruch 1, wobei das eine oder die mehreren Aniontenside ausgewählt sind aus der Gruppe bestehend aus: (1) einem Tensid von linearem oder verzweigtem alkoxyliertem C₁₀-C₂₀-Alkylsulfat (AAS); (2) einem Tensid von linearem oder verzweigtem nichtalkoxyliertem C₆-C₂₀-Alkylsulfat (AS); (3) einem Tensid von linearem C₁₀-C₂₀-Alkylbenzolsulfonat (LAS); und (4) Kombinationen davon.

3. Waschmittelgranulat nach Anspruch 2, wobei der Kern nur ein Tensid umfasst, welches das Tensid von linearem oder verzweigtem alkoxyliertem C₁₀-C₂₀-Alkylsulfat (AAS) ist.

4. Waschmittelgranulat nach Anspruch 2, wobei der Kern das Tensid von linearem oder verzweigtem alkoxyliertem

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C₁₀-C₂₀-Alkylsulfat (AAS) und das Tensid von linearem C₁₀-C₂₀-Alkylbenzolsulfonat (LAS) umfasst, wobei das Gewichtsverhältnis von AAS zu LAS im Bereich von 1:3 bis 10:1, vorzugsweise von 1:2 bis 8:1, stärker bevorzugt von 1:1 bis 5:1, am stärksten bevorzugt von 2:1 bis 4:1 liegt.

- 5 5. Waschmittelgranulat nach einem der Ansprüche 2 bis 4, wobei das AAS-Tensid ein lineares ethoxyliertes C₁₂-C₁₈-Alkylsulfat (AES) mit einem gewichtsdurchschnittlichen Ethoxylierungsgrad von 0,5 bis 3,0, vorzugsweise von 0,5 bis 2, stärker bevorzugt von 0,5 bis 1 ist.
- 10 6. Waschmittelgranulat nach einem der Ansprüche 1 bis 5, wobei das nicht quaternisierte alkoxylierte Polyalkylenimin eine empirische Formel (I) von (PEI)_a-(EO)_b-R₁ aufweist, wobei a das durchschnittliche Zahlenmittel des Molekulargewicht des Polyalkyleniminkerns (MWPEI) des alkoxylierten Polyalkylenimins ist und im Bereich von etwa 100 bis etwa 100.000 Dalton liegt, wobei b der gewichtsdurchschnittliche Ethoxylierungsgrad in der einen oder den mehreren Seitenketten des alkoxylierten Polyalkylenimins ist und im Bereich von etwa 5 bis 40 liegt, und wobei R₁ unabhängig ausgewählt ist aus der Gruppe bestehend aus Wasserstoff, C₁-C₄-Alkyl und Kombinationen davon.
- 15 7. Waschmittelgranulat nach einem der Ansprüche 1 bis 5, wobei das nicht quaternisierte alkoxylierte Polyalkylenimin eine empirische Formel (II) von (PEI)_o-(EO)_m(PO)_n-R₂ oder (PEI)_o-(PO)_n(EO)_m-R₂ aufweist, wobei o das durchschnittliche Zahlenmittel des Molekulargewicht des Polyalkyleniminkerns (MWPEI) des alkoxylierten Polyalkylenimins ist und im Bereich von 100 bis 100.000 Dalton liegt, wobei m der gewichtsdurchschnittliche Ethoxylierungsgrad in der einen oder den mehreren Seitenketten des alkoxylierten Polyalkylenimins ist, der von 10 bis 50 reicht, wobei n der gewichtsdurchschnittliche Propoxylierungsgrad in der einen oder den mehreren Seitenketten des alkoxylierten Polyalkylenimins ist, der von 1 bis 50 reicht, und wobei R₂ unabhängig ausgewählt ist aus der Gruppe bestehend aus Wasserstoff, C₁-C₄-Alkyl und Kombinationen davon.
- 20 8. Waschmittelgranulat nach einem der Ansprüche 1 bis 7, wobei das nicht quaternisierte alkoxylierte Polyethylenimin in einer Menge vorhanden ist, die im Bereich von 0,5 Gew.-% bis 10 Gew.-%, vorzugsweise 1 Gew.-% bis 5 Gew.-%, bezogen auf das Gesamtgewicht des Waschmittelgranulats, liegt.
- 25 9. Waschmittelgranulat nach einem der Ansprüche 1 bis 8, wobei der Kern des Waschmittelgranulats ferner einen festen Träger umfasst, der ausgewählt ist aus der Gruppe bestehend aus: Zeolith, Siliciumdioxid, Carboxymethylcellulose, modifizierter Stärke und Kombinationen davon; wobei vorzugsweise der feste Träger Siliciumdioxid ist; und wobei mehr bevorzugt der feste Träger in einer Menge im Bereich von 5 % bis 50 %, vorzugsweise von 15 % bis 45 %, stärker bevorzugt von 20 % bis 30 %, bezogen auf das Gesamtgewicht des Waschmittelgranulats, vorhanden ist.
- 30 10. Waschmittelgranulat nach einem der Ansprüche 1 bis 9, wobei der Kern des Waschmittelgranulats ferner ein wasserlösliches anorganisches Salz umfasst, das ausgewählt ist aus der Gruppe bestehend aus Natriumsulfat, Kaliumsulfat, Natriumcarbonat, Kaliumcarbonat, Natriumbicarbonat, Kaliumbicarbonat und Kombinationen davon; und wobei vorzugsweise das wasserlösliche anorganische Salz in einer Menge im Bereich von 1 % bis 20 %, vorzugsweise von 2 % bis 15 %, stärker bevorzugt von 3 % bis 10 %, bezogen auf das Gesamtgewicht des Waschmittelgranulats, vorhanden ist.
- 35 11. Waschmittelgranulat nach einem der Ansprüche 1 bis 10, wobei die Beschichtungsschicht von Siliciumdioxid in einer Menge im Bereich von 1 Gew.-% bis 10 Gew.-%, vorzugsweise von 2 Gew.-% bis 5 Gew.-%, bezogen auf das Gesamtgewicht des Waschmittelgranulats, vorhanden ist und wobei das Siliciumdioxid vorzugsweise hydrophiles Siliciumdioxid ist.
- 40 12. Waschmittelgranulat nach einem der Ansprüche 1 bis 11, **gekennzeichnet durch** einen Gesamtfeuchtigkeitsgehalt von nicht mehr als 5 %, vorzugsweise nicht mehr als 3 %, stärker bevorzugt nicht mehr als 2,5 %, bezogen auf das Gesamtgewicht des Waschmittelgranulats.
- 45 13. Granulöse Waschmittelzusammensetzung, umfassend zu 1 % bis 99 % das Waschmittelgranulat nach einem der Ansprüche 1 bis 12.
- 50 14. Verfahren zum Herstellen des Waschmittelgranulats nach einem der Ansprüche 1 bis 12, umfassend die Schritte:
- 55 (a) Bilden einer wässrigen Paste, die das eine oder die mehreren Aniontenside, das nicht quaternisierte alkoxylierte Polyethylenimin und Wasser umfasst;
- (b) Mischen der wässrigen Paste aus Schritt (a) mit einem festen Träger, um ein Kernteilchen zu bilden; und

(c) Beschichten von Siliciumdioxid auf das Kernteilchen.

Revendications

1. Granule de détergent **caractérisé par** une teneur totale en agent tensioactif anionique allant de 40 % à 90 % en poids, ledit granule de détergent comprenant :
 - un noyau qui comprend : (a) un ou plusieurs agents tensioactifs anioniques ; et (b) une polyéthylène-imine alcoylée non quaternisée ayant un noyau polyalkylène-imine avec une ou plusieurs chaînes latérales alcoxy liées à au moins un atome d'azote dans le noyau polyalkylène-imine ; et
 - une couche d'enrobage par-dessus le noyau, ladite couche d'enrobage comprenant de la silice.
2. Granule de détergent selon la revendication 1, dans lequel ledit ou lesdits agents tensioactifs anioniques sont choisis dans le groupe constitué par : (1) un agent tensioactif sulfate alkylalcoylé (AAS) linéaire ou ramifié en C_{10} à C_{20} ; (2) un agent tensioactif sulfate d'alkyle (AS) non alcoylé linéaire ou ramifié en C_6 à C_{20} ; (3) un agent tensioactif sulfonate d'alkylbenzène linéaire (LAS) en C_{10} à C_{20} ; et (4) des combinaisons de ceux-ci.
3. Granule de détergent selon la revendication 2, dans lequel ledit noyau ne comprend qu'un seul agent tensioactif qui est l'agent tensioactif sulfate alkylalcoylé (AAS) linéaire ou ramifié en C_{10} à C_{20} .
4. Granule de détergent selon la revendication 2, dans lequel ledit noyau comprend l'agent tensioactif sulfate alkylalcoylé (AAS) linéaire ou ramifié en C_{10} à C_{20} et l'agent tensioactif sulfonate d'alkylbenzène linéaire (LAS) en C_{10} à C_{20} , le rapport pondéral de l'AAS au LAS allant de 1:3 à 10:1, de préférence de 1:2 à 8:1, plus préférablement 1:1 à 5:1, le plus préférablement de 2:1 à 4:1.
5. Granule de détergent selon l'une quelconque des revendications 2 à 4, dans lequel l'agent tensioactif AAS est un sulfate alkyléthoxylé (AES) linéaire en C_{12} à C_{18} ayant un degré moyen d'éthoxylation en poids allant de 0,5 à 3,0, de préférence de 0,5 à 2, plus préférablement de 0,5 à 1.
6. Granule de détergent selon l'une quelconque des revendications 1 à 5, dans lequel la polyéthylène-imine alcoylée non quaternisée a une formule empirique (I) de $(PEI)a-(EO)b-R_1$, a étant la masse moléculaire moyenne en nombre moyen du noyau polyalkylène-imine (MWPEI) de la polyalkylène-imine alcoylée et étant dans la plage allant d'environ 100 à environ 100 000 Daltons, b étant le degré moyen d'éthoxylation en poids dans ladite ou lesdites chaînes latérales de la polyalkylène-imine alcoylée et étant dans la plage allant d'environ 5 à environ 40, et R_1 étant indépendamment choisi dans le groupe constitué par hydrogène, alkyle en C_1 à C_4 , et combinaisons de ceux-ci.
7. Granule de détergent selon l'une quelconque des revendications 1 à 5, dans lequel la polyéthylène-imine alcoylée non quaternisée a une formule empirique (II) de $(PEI)o-(EO)m-(PO)n-R_2$ ou $(PEI)o-(PO)n-(EO)m-R_2$, o étant la masse moléculaire moyenne en nombre moyen du noyau polyalkylène-imine (MWPEI) de la polyalkylène-imine alcoylée et étant dans la plage allant de 100 à 100 000 Daltons, m étant le degré moyen d'éthoxylation en poids dans ladite ou lesdites chaînes latérales de la polyalkylène-imine alcoylée qui va de 10 à 50, n étant le degré moyen de propoxylation en poids dans ladite ou lesdites chaînes latérales de la polyalkylène-imine alcoylée qui va de 1 à 50, et R_2 étant indépendamment choisi dans le groupe constitué par hydrogène, alkyle en C_1 à C_4 , et combinaisons de ceux-ci.
8. Granule de détergent selon l'une quelconque des revendications 1 à 7, dans lequel la polyéthylène-imine alcoylée non quaternisée est présente en une quantité allant de 0,5 % à 10 %, de préférence 1 % à 5 %, en poids total dudit granule de détergent.
9. Granule de détergent selon l'une quelconque des revendications 1 à 8, dans lequel le noyau dudit granule de détergent comprend en outre un support solide choisi dans le groupe constitué par : zéolite, silice, carboxyméthylcellulose, amidon modifié, et combinaisons de ceux-ci ; dans lequel de préférence ledit support solide est de la silice ; et dans lequel plus préférablement ledit support solide est présent en une quantité allant de 5 % à 50 %, de préférence de 15 % à 45 %, plus préférablement de 20 % à 30 %, en poids total dudit granule de détergent.
10. Granule de détergent selon l'une quelconque des revendications 1 à 9, dans lequel le noyau dudit granule de détergent comprend en outre un sel inorganique hydrosoluble choisi dans le groupe constitué par sulfate de sodium,

sulfate de potassium, carbonate de sodium, carbonate de potassium, bicarbonate de sodium, bicarbonate de potassium, et combinaisons de ceux-ci ; et dans lequel de préférence ledit sel inorganique hydrosoluble est présent en une quantité allant de 1 % à 20 %, de préférence de 2 % à 15 %, plus préférablement de 3 % à 10 %, en poids total dudit granule de détergent.

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11. Granule de détergent selon l'une quelconque des revendications 1 à 10, dans lequel la couche de silice d'enrobage est présente en une quantité allant de 1 % à 10 %, de préférence de 2 % à 5 %, en poids total dudit granule de détergent, et dans lequel de préférence la silice est de la silice hydrophile.

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12. Granule de détergent selon l'une quelconque des revendications 1 à 11, **caractérisé par** une teneur totale en humidité n'excédant pas 5 %, de préférence n'excédant pas 3 %, plus préférablement n'excédant pas 2,5 %, en poids total dudit granule de détergent.

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13. Composition détergente granulaire comprenant de 1 % à 99 % du granule de détergent selon l'une quelconque des revendications 1 à 12.

14. Procédé de fabrication du granule de détergent selon l'une quelconque des revendications 1 à 12, comprenant les étapes consistant à :

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(a) former une pâte aqueuse comprenant le ou les agents tensioactifs anioniques, la polyéthylène-imine alcoylée non quaternisée, et de l'eau ;

(b) le mélange de la pâte aqueuse provenant de l'étape (a) avec un support solide pour former une particule de noyau ; et

(c) l'enrobage de silice par-dessus ladite particule de noyau.

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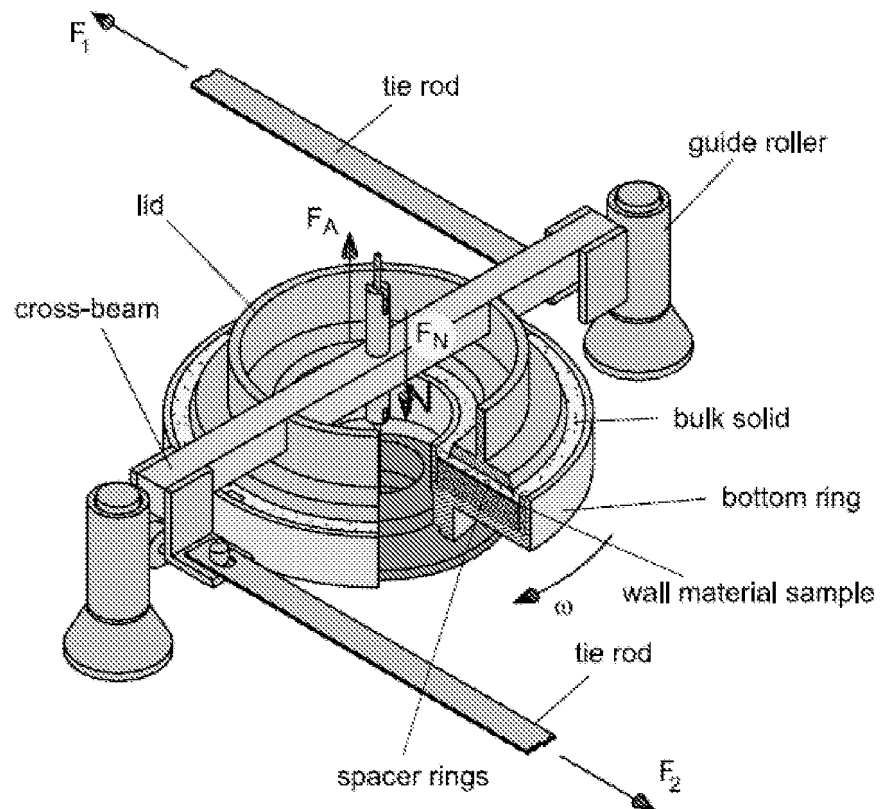


FIG. 1

REFERENCES CITED IN THE DESCRIPTION

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