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

(11) EP 2 297 288 B1

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
08.05.2013 Bulletin 2013/19

(21) Application number: **09793904.5**

(22) Date of filing: **17.06.2009**

(51) Int Cl.:
C11D 3/02 *(2006.01)* ***C11D 3/20*** *(2006.01)*
C11D 3/22 *(2006.01)* ***C11D 17/00*** *(2006.01)*

(86) International application number:
PCT/EP2009/057537

(87) International publication number:
WO 2010/003792 (14.01.2010 Gazette 2010/02)

(54) **LAUNDRY COMPOSITIONS**

WASCHMITTELZUSAMMENSETZUNGEN

COMPOSITIONS DE LAVAGE

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

(30) Priority: **09.07.2008 EP 08160024**

(43) Date of publication of application:
23.03.2011 Bulletin 2011/12

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

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WO-A-2008/083877 **US-A- 5 334 229**

EP 2 297 288 B1

Printed by Jouve, 75001 PARIS (FR)

Description

FIELD OF INVENTION

[0001] This invention relates to an alginate granule. More particularly, the invention is directed to an alginate granule comprising citric acid. The invention further relates to laundry detergent compositions comprising the alginate granules of the invention, to a process to make the alginate granules and to the use of said granules to deliver benefit agents to the fabric.

BACKGROUND

[0002] Encapsulation or immobilisation of active materials is a well known technique which can offer advantages such as the stabilisation/protection of active materials that are otherwise unstable or reactive. Alginates are known as encapsulation materials.

[0003] Our co-pending application WO 2008/083877 relates to gelled alginate beads comprising alginate with a M:G ratio of from 0.1:1 to less than 1:1; one or more cationic species and one or more benefit agents. These are used to slowly release a benefit agent.

[0004] Another example of encapsulate use of alginate can be found in WO 00/46337 (Quest International B.V.). This document relates to a liquid detergent composition containing greater than 5% by weight of surfactant and an encapsulate containing greater than 10% by weight of active material and a cross-linked anionic gum. The anionic gum can be an alginate, and the active material can be a fragrance.

[0005] WO 2007/009621 discloses fabric softening particles which incorporate a fabric softening emulsion into an alginate or carrageenan polysaccharide matrix. These particles do not contain any sequestrant. The alginate particles leave residues cn fabric due to the reliance on sequestrants present in detergent formulations to aid dissolution of the softening particle.

[0006] WO 2004/074422 A discloses a sprayable, acidic, hard surface cleaning and/or disinfecting composition which contains suspended inclusions which appear as visibly discernible, discrete particulate materials, preferably where said discrete particulate materials are based on alginates which are present as two or more classes of particulate materials.

[0007] US 5, 334, 229 discloses alginate gel beads useful for encapsulating plant reproductive units, and a method for production thereof.

[0008] A problem that exists with such alginate encapsulates/beads is that they leave visible residues on laundered clothes. Such visible residues are not only problematic for consumers, but are also indicative that the alginate matrix has not released the encapsulated benefit agent or other active material.

SUMMARY OF INVENTION

[0009] We have found that inclusion of citric acid in the granulation process provides alginate granules that exhibit a reduced level of visible residues in laundry use.

[0010] In one aspect the present invention provides an alginate granule comprising:

(a) 30-80 wt.% of alginate;
(b) 10-30 % of one or more cationic species which is a divalent or polyvalent metal cation;
(c) 5-30 % of citric acid; and
(d) one or more fabric benefit agents.

[0011] A second aspect of the invention provides a laundry detergent composition comprising from 0.1 to 25 wt.% of the alginate granule of the first aspect, from 2 to 70 wt.% of a surfactant, and from 1 to 70 wt.% of a builder.

[0012] A third aspect of the invention provides the use of the alginate granule of first aspect, to deliver a fabric benefit agent to a textile during the laundering process.

[0013] A fourth aspect of the invention provides a process for making the alginate granules of the first aspect, wherein the process includes the steps of:-

a) provision of a first solution comprising an admixture of alginate, citric acid, and one or more benefit agents;
b) forming droplets of the first solution; and,
c) contacting said droplets with a second solution comprising a cationic species which is a divalent or polyvalent metal cation.

DETAILED DESCRIPTION OF THE INVENTION

[0014] The amounts of components present in the various compositions quoted herein are given as wt.% of the composition unless otherwise stated.

[0015] Except in the operating and comparative examples, or where otherwise explicitly indicated, all numbers in this description indicating amounts or ratios of material or conditions of reaction, physical properties of materials and/cr use are to be understood as modified by the word "about".

Alginate Granules

[0016] The alginate granules preferably have a size range of from 0.05 to 10mm. More preferably the particle size is between 0.1 and 2mm. The granule size can be measured for example using graded sieves.

[0017] The alginate granule comprises:

(a) 30-80 wt.% of alginate;
(b) 10-30% of one or more cationic species which is a divalent or polyvalent metal cation;
(c) 5-30% citric acid; and,
(d) one or more fabric benefit agents.

Alginate

[0018] "Alginate" is the general name for alginic acid and its salts. Alginates are linear polysaccharides made up from β-1,4 linked D-mannuronate (M) residues and its C-5 epimer, α-1,4 linked L-guluronate (G) residues. The alginates have a block polymeric arrangement of these M and G residues along the linear chain. The arrangement of these blocks can be described as being blocks of repeating M residues, repeating G residues, or alternating M and G residues.

[0019] The ratio of mannuronate to guluronate residues present in the alginate is well known in the art as the M:G ratio. The M:G ratio of the alginate can vary due to the source or growth conditions of the alginate. One common alginate source is brown seaweed *(Phaeophyceae).*

[0020] The M:G ratio of the alginate used in the present invention is preferably from 0.1:1 to less than 1:1, for example 0.1:1 to 0.99:1. This means that the alginates used herein preferably contain a greater number of G residues than M residues. The M:G ratio is more preferably 0.1:1 to 0.8:1, even more preferably from 0.2:1 to 0.8:1. Certain embodiments of the alginate granules of the present invention may comprise alginate having an M:G ratio of from 0.25 to 0.75. Suitable sources for these alginates are those obtained from the fronds and stipes of *Laminaria hyperborea.*

[0021] The alginate granules comprise preferably alginate with a M:G as defined above. More preferably all of the alginate present in the granule has the aforementioned M:G ratios.

[0022] Depending on the nature of the benefit agents and the release profile required, the molecular weight of the alginate can be between 1,000 to 3,000,000 Daltons.

[0023] Conveniently, the alginate is used in the form of a sodium salt.

[0024] Suitable alginates with the preferred M:G ratio are available under the "Manugel" trade name from International Speciality Products, for example "Manugel GMB"; "Protonal" from FMC Biopolymer; and, "Satialgine", "Cecalgum" and "Algogel" from Texturant Systems.

[0025] The alginate is present in the granule at a level of from 30 to 80 wt.%.

Cationic Species

[0026] The cationic species form the gelled cross-linked matrix with the alginate. The cationic species is a divalent or polyvalent metal cation. The cationic species forms a gelled network with alginate. In a preferred embodiment, the cationic species is a calcium salt (e.g. calcium chloride).

[0027] The cationic species is present in the granule at a level of fron 10 to 30 wt.%.

Citric acid

[0028] Citric acid as used herein incorporates the free acid itself as well as its various anionic forms. Preferably the citric acid is incorporated in the alginate granule as the free acid.

[0029] The citric acid is present in the granule at a level of from 5 to 30 wt.%.

Fabric benefit agents

[0030] Preferably the fabric benefit agent is selected from the group consisting of: chlorine/oxygen scavengers, anti-oxidants, non-calcium binding sequestrants, perfumes, antimicrobial agents, antibacterial agents, antifungal agents, lubricants, UV absorbers, shading dyes, fluorescent whitening agents, dispersants, anti-redeposition agents, soil release agents, enzymes (for removing fuzz or pills or preventing staining), dye transfer inhibitors, dye binders, dye fixers, softeners, or crystal growth inhibitors. The fabric benefit agent may also be a mixture of two or more of the aforementioned benefit agents.

[0031] Most preferably the fabric benefit agent is selected from the group consisting of: mild reducing agents, non-calcium binding sequestrants, perfumes, fluorescent whitening agents, shading dyes, antimicrobial agents or mixtures thereof.

[0032] The inclusion level of the fabric benefit agent(s) in the granules is dependant on the amount that is required to achieve the benefit required, the release profile of the agent(s) and the calcium level. Typical ranges of fabric benefit agents in the alginate granule are from 0.001 to 60wt.% of the granule.

[0033] For certain fabric benefit agents such as perfumes, fluorescent whitening agents cr shading dyes which are effective at low levels, the inclusion level can preferably be between 0.001% to 20wt.% of the granule.

Process for making the granules

[0034] A suitable process for making the alginate granules of the invention includes the steps of:-

a) provision of a first solution comprising an admixture of alginate, citric acid, and one or more benefit agents;
b) forming droplets of the first solution; and,
c) contacting said droplets with a second solution comprising a cationic species which is a divalent or polyvalent metal cation.

[0035] This is an example of a diffusion setting method and can suitably be carried out at neutral pH.

[0036] In an alternative process, citric acid is also present in the second solution.

[0037] The solution can use any suitable solvent. Water is preferred.

Laundry Detergent Composition

[0038] The alginate granule is suitably delivered to the fabric via incorporation into laundry detergent composition.

[0039] Suitable laundry detergent compositions comprise from 0.1 to 25 wt.% of the alginate granule and from 2 to 70 wt.% of a surfactant and from 1 to 70 wt.% of a builder.

[0040] The alginate granules are present in the laundry detergent composition at a level of from 0.1 to 25 wt.%, preferably from 0.5 to 10 wt.%.

[0041] The laundry treatment composition may take the form of an isotropic liquid, a surfactant-structured liquid, a granular, spray-dried or dry-blended powder, a tablet, a paste, a molded solid or any other laundry detergent form known to those skilled in the art. The composition is preferably a liquid or granular laundry composition, most preferably a granular laundry composition.

[0042] Preferred laundry detergent composition forms which are particularly suitable in combination with the alginate granules of the invention are granular, spray-dried or dry-blended powder compositions.

SURFACTANT

[0043] The laundry detergent composition comprises between 2 to 70 wt.% of a surfactant, most preferably 10 to 30 wt.%. In general, the nonionic and anionic surfactants of the surfactant system may be chosen from the surfactants described "Surface Active Agents" Vol. 1, by Schwartz & Perry, Interscience 1949, Vol. 2 by Schwartz, Perry & Berch, Interscience 1958, in the current edition of "McCutcheon's Emulsifiers and Detergents" published by Manufacturing Confectioners Company or in "Tenside-Taschenbuch", H. Stache, 2nd Edn., Carl Hauser Verlag, 1981. Preferably the surfactants used are saturated.

[0044] Suitable nonionic detergent compounds which may be used include, in particular, the reaction products of compounds having a hydrophobic group and a reactive hydrogen atom, for example, aliphatic alcohols, acids, amides or alkyl phenols with alkylene oxides, especially ethylene oxide either alone or with propylene oxide. Specific nonionic detergent compounds are C_6 to C_{22} alkyl phenol-ethylene oxide condensates, generally 5 to 25 EO, i.e. 5 to 25 units of ethylene oxide per molecule, and the condensation products of aliphatic C_8 to C_{18} primary or secondary linear or branched alcohols with ethylene oxide, generally 5 to 40 EO.

[0045] Suitable anionic detergent compounds which may be used are usually water-soluble alkali metal salts of organic sulphates and sulphonates having alkyl radicals containing from about 8 to about 22 carbon atoms, the term alkyl being used to include the alkyl portion of higher acyl radicals. Examples of suitable synthetic anionic detergent compounds are sodium and potassium alkyl sulphates, especially those obtained by sulphating higher C_8 to C_{18} alcohols, produced for example from tallow or coconut oil, sodium and potassium alkyl C_9 to C_{20} benzene sulphonates, particularly sodium linear secondary alkyl C_{10} to C_{15} benzene sulphonates; and sodium alkyl glyceryl ether sulphates, especially those ethers of the higher alcohols derived from tallow or coconut oil and synthetic alcohols derived from petroleum. The preferred anionic detergent compounds are sodium C_{11} to C_{15} alkyl benzene sulphonates and sodium C_{12} to C_{18} alkyl sulphates. Also applicable are surfactants such as those described in EP-A-328 177 (Unilever), which show resistance to salting-out, the alkyl polyglycoside surfactants described in EP-A-070 074, and alkyl monoglycosides.

[0046] Preferred surfactant systems are mixtures of anionic with nonionic detergent active materials, in particular the groups and examples of anionic and nonionic surfactants pointed out in EP-A-346 995 (Unilever). Especially preferred is surfactant system that is a mixture of an alkali metal salt of a C_{16} to C_{18} primary alcohol sulphate together with a C_{12} to C_{15} primary alcohol 3 to 7 EO ethoxylate.

[0047] The nonionic detergent is preferably present in amounts greater than 10%, e.g. 25 to 90 wt.% of the surfactant system. Anionic surfactants can be present for example in amounts in the range from about 5 wt.% to about 40 wt.% of the surfactant system.

BUILDERS OR COMPLEXING AGENTS

[0048] The laundry detergent composition may comprise from 1 to 70 wt.% of a builder.

[0049] For laundry compositions in the form of granular, spray-dried or dry-blended powders, the level of builder is preferably from 1 to 40 wt.%.

[0050] Builder materials may be selected from 1) calcium sequestrant materials, 2) precipitating materials, 3) calcium ion-exchange materials and 4) mixtures thereof.

[0051] It is preferred that when an insoluble inorganic builder, e.g., zeolite is used, the size is in the range 0.1 to 10 microns (as measured by The Mastersizer 2000 particle size analyzer using laser diffraction ex Malvern™).

[0052] Examples of calcium sequestrant builder materials include alkali metal polyphosphates, such as sodium tripolyphosphate and organic sequestrants, such as ethylene diamine tetraacetic acid.

[0053] Examples of precipitating builder materials include sodium orthophosphate and sodium carbonate.

[0054] Examples of calcium ion-exchange builder materials include the various types of water-insoluble crystalline or amorphous aluminosilicates, of which zeolites are the best known representatives, e.g. zeolite A, zeolite B (also known as zeolite P), zeolite C, zeolite X, zeolite Y and also the zeolite P-type as described in EP-A-0,384,070.

[0055] The composition may also contain 0-50 wt.% of a builder or complexing agent such as ethylenediaminetetraacetic acid, diethylenetriamine-pentaacetic acid, alkyl- or alkenylsuccinic acid, nitrilotriacetic acid or the other builders mentioned below. Many builders are also bleach-stabilising agents by virtue of their ability to complex metal ions.

[0056] Zeolite and carbonate (including bicarbonate and sesquicarbonate) are preferred builders.

[0057] The composition may contain as builder a crystalline aluminosilicate, preferably an alkali metal aluminosilicate, more preferably a sodium aluminosilicate. This is typically present at a level of less than 15 wt.%. Aluminosilicates are materials having the general formula:

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

where M is a monovalent cation, preferably sodium. These materials contain some bound water and are required to have a calcium ion exchange capacity of at least 50 mg CaO/g. The preferred sodium aluminosilicates contain 1.5-3.5 SiO_2 units in the formula above. They can be prepared readily by reaction between sodium silicate and sodium aluminate, as amply described in the literature. The ratio of surfactants to aluminosilicate (where present) is preferably greater than 5:2, more preferably greater than 3:1.

[0058] Alternatively, or additionally to the aluminosilicate builders, phosphate builders may be used. In this art the term 'phosphate' embraces diphosphate, triphosphate, and phosphonate species. Other forms of builder include silicates, such as soluble silicates, metasilicates, layered silicates (e.g. SKS-6 from Hoechst).

[0059] Preferably the laundry detergent formulation is a non-phosphate built laundry detergent formulation, i.e., contains less than 1 wt.% of phosphate.

SHADING AGENT

[0060] The laundry detergent composition preferably comprises a blue or violet shading agent in the range from 0.0001 to 0.01 wt.%. The shading agents reduce the perception of damage to many coloured garments and increase whiteness

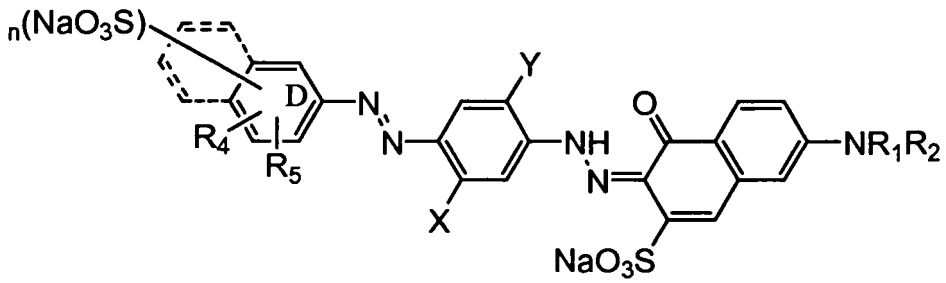
of white garments.

[0061] The shading agents are preferably selected from blue and violet dyes of the solvent disperse basic, direct and acid type listed in the colour index (Society of Dyers and Colourists and American Association of Textile Chemists and Colorists 2002).

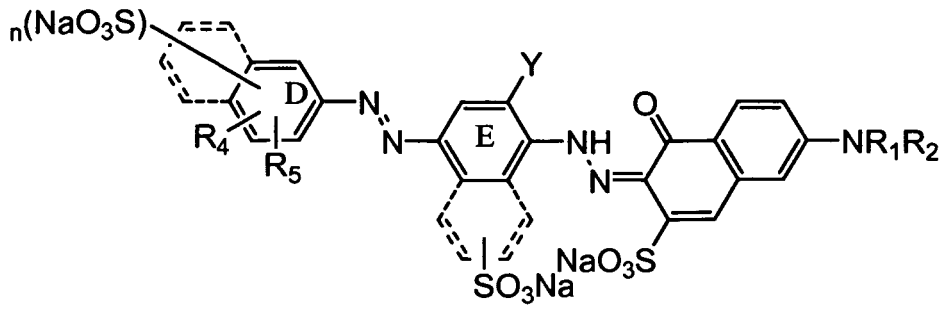
[0062] Preferably a direct violet or direct blue dyes is present. Preferably the dyes are bis-azo, tris-azo dyes or triphendioxazine dye. The carcinogenic benzidene based dyes are not preferred.

[0063] Bis-azo copper containing dyes such as direct violet 66 may be used.

[0064] The most preferred bis-azo dyes have the following structure:



or



wherein:

ring D and E may be independently naphthyl or phenyl as shown;
R_1 is selected from: hydrogen and C1-C4-alkyl, preferably hydrogen;
R_2 is selected from: hydrogen, C1-C4-alkyl, substituted or unsubstituted phenyl and substituted or unsubstituted naphthyl, preferably phenyl;
R_3 and R_4 are independently selected from: hydrogen and C1-C4-alkyl, preferably hydrogen or methyl;
X and Y are independently selected from: hydrogen, C1-C4-alkyl and C1-C4-alkoxy; preferably the dye has X= methyl; and, Y = methoxy and n is 0, 1 or 2, preferably 1 or 2.

[0065] Preferred bis-azo dyes are direct violet 7, direct violet 9, direct violet 11, direct violet 26, direct violet 31, direct violet 35, direct violet 40, direct violet 41, direct violet 51, and direct violet 99.

[0066] Preferred solvent and disperse dyes, are selected from, mono-azo or anthraquinone dyes, most preferably, solvent violet 13, disperse violet 27 disperse violet 26, disperse violet 28, disperse violet 63 and disperse violet 77.

[0067] A preferred pigment is pigment violet 23.

ENZYMES

[0068] The laundry detergent composition preferably comprises one or more enzymes which provide cleaning performance and/or fabric care benefits. Examples of suitable enzymes include, but are not limited to, hemicellulases, peroxidases, proteases, cellulases, xylanases, lipases, phospholipases, esterases, cutinases, pectinases, mannanases, pectate lyases, keratinases, reductases, oxidases, phenoloxidases,-lipoxygenases, ligninases, pullulanases, tannases, pentosanases, malanases, arabinosidases, hyaluronidase, chondroitinase, laccase, and amylases, or mixtures thereof. A typical combination is an enzyme cocktail that may comprise, for example, a protease and lipase in conjunction with amylase. When present in a cleaning composition, the aforementioned additional enzymes may be present at levels from about 0.00001 wt.% to about 2 wt.%, from about 0.0001 wt.% to about 1 wt.% or even from about 0.001 wt.% to

about 0.5 wt.% enzyme protein by weight of the composition.

[0069] Preferred enzymes are cellulases.

FLUORESCENT AGENT

[0070] The laundry detergent composition preferably comprises a fluorescent agent (optical brightener). Fluorescent agents are well known and many such fluorescent agents are available commercially. Usually, these fluorescent agents are supplied and used in the form of their alkali metal salts, for example, the sodium salts. The total amount of the fluorescent agent or agents used in the composition is generally from 0.005 to 2 wt.%, more preferably 0.01 to 0.1 wt. %. Preferred classes of fluorescer are: Di-styryl biphenyl compounds, e.g. Tinopal (Trade Mark) CBS-X, Diamine stilbene di-sulphonic acid compounds, e.g. Tinopal DMS pure Xtra and Blankophor (Trade Mark) HRH, and Pyrazoline compounds, e.g. Blankophor SN. Preferred fluorescers are: sodium 2-(4-styryl-3-sulfophenyl)-2H-napthol[1,2-d]trazole, 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-sulfoslyryl)biphenyl.

PERFUME

[0071] Preferably the laundry detergent composition comprises a perfume. The perfume is preferably in the range from 0.001 to 3 wt.%, most preferably 0.1 to 1 wt.%. Many suitable examples of perfumes are provided in the CTFA (Cosmetic, Toiletry and Fragrance Association) 1992 International Buyers Guide, published by CFTA Publications and OPD 1993 Chemicals Buyers Directory 80th Annual Edition, published by Schnell Publishing Co.

[0072] It is commonplace for a plurality of perfume components to be present in a formulation. In the compositions of the present invention it is envisaged that there will be four or more, preferably five or more, more preferably six or more or even seven or more different perfume components.

[0073] In perfume mixtures preferably 15 to 25 wt.% are top notes. Top notes are defined by Poucher (Journal of the Society of Cosmetic Chemists 6(2):80 [1955]). Preferred top-notes are selected from citrus oils, linalool, linalyl acetate, lavender, dihydromyrcenol, rose oxide and cis-3-hexanol.

[0074] Perfume and top note may be used to cue the whiteness benefit of the invention.

POLYMERS

[0075] The laundry detergent composition may comprise one or more polymers. Examples are carboxymethylcellulose, poly(ethylene glycol), poly(vinyl alcohol), polycarboxylates such as polyacrylates, maleic/acrylic acid copolymers and lauryl methacrylate/acrylic acid copolymers.

HYDROTROBE

[0076] For compositions in the form of a liquid, it is useful to include a hydrotrope, which prevents liquid crystal formation. The addition of the hydrotrope thus aids the clarity/transparency of the composition. Suitable hydrotropes include but are not limited to propylene glycol, ethanol, urea, salts of benzene sulphonate, toluene sulphonate, xylene sulphonate or cumene sulphonate. Suitable salts include but are not limited to sodium, potassium, ammonium, monoethanolamine, triethanolamine. Preferably, the hydrotrope is selected from the group consisting of propylene glycol, xylene sulfonate, ethanol, and urea to provide optimum performance. The amount of the hydrotrope is generally in the range of from 0 to 30%, preferably from 0.5 to 30%, more preferably from 0.5 to 30%, most preferably from 1 to 15%.

BLEACH

[0077] The laundry detergent compositions may also suitably contain a bleach system. If bleach is present, then it is preferred that the compositions of the invention contain peroxy bleach compounds capable of yielding hydrogen peroxide in aqueous solution, for example inorganic or organic peroxyacids, and inorganic persalts such as the alkali metal perborates, percarbonates, perphosphates, persilicates and persulphates. Bleach ingredients are generally post-dosed as powders.

[0078] If present, the peroxy bleach compound, for example sodium percarbonate, is suitably present in an amount of from 5 to 35 wt.%, preferably from 10 to 25 wt.%. The peroxy bleach compound, for example sodium percarbonate, may be used in conjunction with a bleach activator (bleach precursor) to improve bleaching action at low wash temperatures. The bleach precursor is suitably present in an amount of from 1 to 8 wt.%, preferably from 2 to 5 wt.%.

[0079] Preferred bleach precursors are peroxycarboxylic acid precursors, more especially peracetic acid precursors

and peroxybenzoic acid precursors; and peroxycarbonic acid precursors. An especially preferred bleach precursor suitable for use in the present invention is N, N, N', N'-tetracetyl ethylenediamine (TAED).

[0080] A bleach stabiliser (heavy metal sequestrant) may also be present. Suitable bleach stabilisers include ethylenediamine tetraacetate (EDTA), ethylenediamine disuccinate (EDDS), and the aminopolyphosphonates such as ethylenediamine tetramethylene phosphonate (EDTMP) and diethylenetriamine pentamethylene phosphonate (DETPMP).

Experimental

Example 1

[0081] Three granules were prepared using the diffusion setting process.

Batch 1:

[0082]

Alginate solution - 200ml demineralised water + 4.5g Manugel GMB + 0.1013g Acid Blue 80

Hardening bath - 500ml demineralised water + 1.75g $CaCl_2.2H_2O$ + 0.2533g Acid Blue 80

Batch 2:

[0083]

Alginate solution - 200ml demineralised water + 4.5g Manugel GMB + 1g Citric acid + 0.1013g Acid Blue 80

Hardening bath - 500ml demineralised water + 1.75g $CaCl_2.2H_2O$ + 2.5g citric acid + 0.2533g Acid Blue 80

Batch 3:

[0084]

Alginate solution - 200ml demineralised water + 4.5g Manugel GMB + 1g Citric acid + 0.1013g Acid Blue 80

Hardening bath - 500ml demineralised water + 1.75g $CaCl_2.2H_2O$ + 10.0g citric acid + 0.2533g Acid Blue 80

[0085] The granules were then removed from the hardening bath using a 1mm sieve and oven dried at 60°C to constant weight.

Release of Benefit Agent Test

[0086] The benefit agent release profile of the three batches of the alginate granules was then measured by placing 1g of granules into 500ml demineralised water adjusted to either pH 4, 7 or 10. The solution was pumped thorough a 10mm quartz flowcell mounted in a Hewlett-Packard 8453 diode array Uv/Vis Spectrophotometer®. The release of Acid Blue 80 was measured by absorption at 629nm over a period of 90 minutes at room temperature.

Time (mins)	Batch 1 pH 7	Batch 2 pH 4	Batch 2 pH 7	Batch 2 pH 10	Batch 3 pH 4	Batch 3 pH 7	Batch 3 pH 10
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000
10	0.134	0.297	0.321	0.469	0.564	0.579	0.829
20	0.206	0.432	0.473	0.718	0.802	0.826	1.141
30	0.248	0.549	0.603	0.937	0.918	0.942	1.311
40	0.276	0.660	0.721	1.252	0.989	1.013	1.399
50	0.302	0.762	0.833	1.456	1.042	1.065	1.444

(continued)

Time (mins)	Batch 1 pH 7	Batch 2 pH 4	Batch 2 pH 7	Batch 2 pH 10	Batch 3 pH 4	Batch 3 pH 7	Batch 3 pH 10
60	0.312	0.858	0.939	1.629	1.083	1.106	1.468
70	0.325	0.950	1.037	1.772	1.118	1.141	1.481
80	0.336	1.034	1.124	1.815	1.148	1.170	1.486
90	0.345	1.034	1.124	1.815	1.173	1.193	1.491
% released	17.3	51.8	56.2	90.8	58.7	59.7	74.6

[Acid Blue 80] released in g/ml - 2.0g/ml = 100% release

[0087] Thus, at pH 10, where the citric acid is converted to sodium citrate, dye release increases significantly compared to pH 4 and pH 7.

Example 2 - Visible Residues Test

[0088] Granule dissolution in a washing machine was assessed using the "black sachet" test, which reproduces the conditions experienced by a granule if it becomes caught in a pocket and is thus suffers less mechanical abrasion than if it was mobile inside the drum.

[0089] 1g of the various alginate granules was placed in between two pieces of black woven cotton and all edges overlocked, thus preventing the alginate granules from escaping. The sachet was then attached to a 100x50cm panel of woven cotton sheeting to prevent it becoming lodged in the door seal of the washing machine. The panel was then placed in a washing machine along with 800g woven cotton sheeting, 800g of knitted cotton and 800g of 65:35 woven cotton:polyester.

[0090] 100g of Persil® Biological washing powder which comprises sodium citrate was placed in the detergent compartment and a 40°C cotton wash cycle carried out (Prenton water, 26°FH). On completion of the wash, the load was removed and tumble dried. The sachet was then opened and the degree of residues assessed on a scale of 1 to 5 (1 = no residues, 5 = high residues).

Batch 1 (no citric acid)	Ranking = 5
Batch 2 (low citric acid)	Ranking = 2
Batch 3 (high citric acid)	Ranking = 1

[0091] As Persil® Biological powder contains sodium citrate, it is clear that inclusion of the sodium citrate (a sequestrant) in the detergent composition is insufficient to stop residues. This confirms the disclosure of WO 2007/009621. The particles of batch 1 are considered a fair representation of the disclosure of WO 2007/009621, in that they contain alginate, benefit agent and calcium. The particles of batches 2 and 3 are according to the invention, and show the benefit of adding citric acid as part of the actual particle, as opposed to relying on sequestrant present in the detergent compositions to aid dissolution of the particle.

[0092] The alginate granules that contained citric acid as part of the granule itself exhibited significantly improved performance in that there were reduced or no residues after washing. This the technical advantage in terms of reduced residues for the incorporation of citric acid in a granule according to the invention as opposed to the prior art disclosures.

Claims

1. An alginate granule comprising:

(a) 30-80 wt.% of alginate;
(b) 10-30% of one or more cationic species which is a divalent or polyvalent metal cation;
(c) 5-30% of citric acid; and
(d) one or more fabric benefit agents.

2. An alginate granule according to claim 1, wherein the alginate has a ratio of mannuronate to guluronate residues (the M:G ratio) of from 0.1:1 to less than 1:1, preferably from 0.1:1 to 0.8:1, more preferably from 0.2:1 to 0.8:1.

3. An alginate granule according to claim 1 or claim 2, wherein the cationic species is calcium.

4. An alginate granule according to any preceding claim, wherein the fabric benefit is selected from the group consisting of: chlorine/oxygen scavengers, antioxidants, non-calcium binding sequestrants, perfumes, antimicrobial agents, antibacterial agents, antifungal agents, lubricants, UV absorbers, shading dyes, fluorescent whitening agents, dispersants, anti-redeposition agents, soil release agents, enzymes (for removing fuzz or pills or preventing staining), dye transfer inhibitors, dye sequestrants, dye fixers, softeners, crystal growth inhibitors, or mixtures thereof.

5. An alginate granule according to claim 4, wherein the fabric benefit is selected from the group consisting of: mild reducing agents, sequestrants, perfumes, fluorescent whitening agents, shading dyes, antimicrobial agents or mixtures thereof.

6. An alginate granule according to any preceding claim wherein the fabric benefit agent is water soluble.

7. A laundry detergent composition comprising:-

(i) from 0.1 to 25 wt.% of the alginate granule of any one of claims 1 to 6,
(ii) from 2 to 70 wt.% of a surfactant; and,
(iii) from 1 to 70 wt.% of a builder.

8. Use of the alginate granule of any one of claims 1 to 6, to deliver a fabric benefit agent to a textile during the laundering process.

9. A process for making the granule of any one of claims 1 to 6, comprising the following steps:-

a) provision of a first solution comprising an admixture of alginate, citric acid, and one or more benefit agents;
b) forming droplets of the first solution; and,
c) contacting said droplets with a second solution comprising a cationic species which is a divalent or polyvalent metal cation.

10. A process according to claim 9, wherein the alginate has a ratio of mannuronate to guluronate residues (the M:G ratio) of from 0.1:1 to less than 1:1.

Patentansprüche

1. Alginatgranulat, das Folgendes aufweist:

(a) 30 bis 80 Gew.-% Alginat;
(b) 10 bis 30 % einer oder mehrerer kationischer Arten, die ein zweiwertiges oder mehrwertiges Metallkation sind;
(c) 5 bis 30 % Citronensäure; und
(d) ein oder mehrere für Textilerzeugnisse vorteilhafte Mittel.

2. Alginatgranulat nach Anspruch 1,
wobei das Alginat ein Verhältnis zwischen Mannuronat- und Guluronatresten (Verhältnis M:G) von 0,1:1 1 bis weniger als 1:1, vorzugweise von 0,1:1 1 bis 0,8:1, stärker bevorzugt von 0,2:1 bis 0,8:1 hat.

3. Alginatgranulat nach Anspruch 1 oder Anspruch 2,
wobei die kationische Art Calcium ist.

4. Alginatgranulat nach einem der vorstehenden Ansprüche,
wobei das für Textilerzeugnisse vorteilhafte Mittel aus der Gruppe ausgewählt ist, bestehend aus: Chlor/Sauerstoff-Scavengern, Antioxidantien, kein Calcium bindenden Komplexbildnern, Duftstoffen, antimikrobiellen Mitteln, antibakteriellen Mitteln, antifungalen Mitteln, Gleitmitteln, UV-Absorbtionsmitteln, Nuancierfarbstoffen, fluoreszierenden Aufhellern, Dispersionsmitteln, die erneute Ablagerung verhindernden Mitteln, schmutzablösenden Mitteln, Enzy-

men (zum Entfernen von Faserflaum oder Knötchen oder zum Verhindern einer Verfärbung), Farbübertragungsinhibitoren, Farbstoff-Komplexbildnern, Farbfixiermitteln, Weichmachern, Inhibitoren für das Kristallwachstum oder Gemischen davon.

5. Alginatgranulat nach Anspruch 4,
wobei das für Textilerzeugnisse vorteilhafte Mittel aus der Gruppe ausgewählt ist, bestehend aus: milden Reduktionsmitteln, Komplexbildnern, Duftstoffen, fluoreszierenden Aufhellern, Nuancierfarbstoffen, antimikrobiellen Mitteln oder Gemischen davon.

6. Aligantgranulat nach einem der vorstehenden Ansprüche,
wobei das für Textilerzeugnisse vorteilhafte Mittel wasserlöslich ist.

7. Waschmittelzusammensetzung, die Folgendes aufweist:

(i) 0,1 bis 25 Gew.-% des Alginatgranulats nach einem der Ansprüche 1 bis 6,
(ii) 2 bis 70 Gew.-% eines Tensids und
(iii) 1 bis 70 Gew.-% eines Builders.

8. Verwendung des Alginatgranulats nach einem der Ansprüche 1 bis 6, um Textilien während eines Waschprozesses ein für Textilerzeugnisse vorteilhaftes Mittel zuzuführen.

9. Verfahren zum Herstellen des Granulats nach einem der Ansprüche 1 bis 6,
das die folgenden Schritte aufweist:

a) Bereitstellen einer ersten Lösung, die ein Gemisch von Alginat, Citronensäure und einem oder mehreren vorteilhaften Mitteln aufweist;
b) Erzeugen von Tröpfchen der ersten Lösung; und
c) Inkontaktbringen der Tröpfchen mit einer zweiten Lösung, die eine kationische Art aufweist, die ein zweiwertiges oder mehrwertiges Metallkation ist.

10. Verfahren nach Anspruch 9,
wobei das Alginat ein Verhältnis zwischen Mannuronat- und Guluronatresten (Verhältnis M:G) von 0,1:1 1 bis wenige als 1:1 aufweist.

Revendications

1. Granule d'alginate comprenant :

(a) de 30 à 80 % en poids d'alginate ;
(b) de 10 à 30 % d'une ou plusieurs espèces cationiques qui sont un cation métallique divalent ou polyvalent ;
(c) de 5 à 30 % d'acide citrique ; et
(d) un ou plusieurs agents bénéfiques pour les tissus.

2. Granule d'alginate selon la revendication 1, dans lequel l'alginate possède un rapport de résidu mannuronate au résidu guluronate (rapport M:G) de 0,1:1 à moins de 1:1, de préférence de 0,1:1 à 0,8:1, plus préférablement de 0,2:1 à 0,8:1.

3. Granule d'alginate selon la revendication 1 ou la revendication 2, dans lequel l'espèce cationique est le calcium.

4. Granule d'alginate selon l'une quelconque des revendications précédentes, dans lequel l'agent bénéfique pour les tissus est choisi dans le groupe constitué par : les piégeurs de chlore/oxygène, les antioxydants, les séquestrants de liaison non calciques, les parfums, les agents antimicrobiens, les agents antibactériens, les agents antifongiques, les lubrifiants, les absorbeurs d'UV, les colorants de nuançage, les agents de blanchiment fluorescents, les dispersants, les agents antiredéposition, les agents anti-salissures, les enzymes (pour éliminer les duvets ou les bouloches ou empêcher les tâches), les inhibiteurs de transfert de colorant, les séquestrants de colorant, les fixateurs de colorant, les assouplissants, les inhibiteurs de la croissance de cristaux, ou des mélanges de ceux-ci.

5. Granule d'alginate selon la revendication 4, dans lequel l'agent bénéfique pour les tissus est choisi dans le groupe constitué par : les agents de réduction doux, les séquestrants, les parfums, les agents de blanchiment fluorescents, les colorants de nuançage, les agents antimicrobiens ou des mélanges de ceux-ci.

6. Granule d'alginate selon l'une quelconque des revendications précédentes, dans lequel l'agent bénéfique pour les tissus est soluble dans l'eau.

7. Composition détergente pour le linge comprenant :

(i) de 0,1 à 25 % en poids du granule d'alginate selon l'une quelconque des revendications 1 à 6,
(ii) de 2 à 70 % en poids d'un tensioactif ; et
(iii) de 1 à 70 % en poids d'un adjuvant.

8. Utilisation d'un granule d'alginate selon l'une quelconque des revendications 1 à 6, pour délivrer un agent bénéfique pour les tissus sur un textile pendant le procédé de lavage du linge.

9. Procédé de préparation d'un granule d'alginate selon l'une quelconque des revendications 1 à 6, comprenant les étapes suivantes :

a) approvisionnement d'une première solution comprenant un mélange d'alginate, d'acide citrique, et d'un ou plusieurs agents bénéfiques ;
b) formation de gouttelettes de la première solution ; et
c) mise en contact desdites gouttelettes avec une seconde solution comprenant une espèce cationique qui est un cation métallique divalent ou polyvalent.

10. Procédé selon la revendication 9, dans lequel l'alginate possède un rapport de résidu mannuronate au résidu guluronate (rapport M:G) de 0,1:1 1 à moins de 1:1.

REFERENCES CITED IN THE DESCRIPTION

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