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(54) **LAUNDRY COMPOSITIONS**

WASCHMITTEL

COMPOSITIONS DE LAVAGE DU LINGE

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(56) References cited:
EP-A- 1 632 560
WO-A-00/46337
WO-A-01/21536
WO-A-97/14780
WO-A-03/002160
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Description

FIELD OF THE INVENTION

[0001] This invention relates to a gelled alginate bead. More particularly, the invention is directed to a gelled alginate bead comprising a certain ratio of D-mannuronate (M) to L-guluronate (G) residues, and to a process for making said bead. The invention further relates to laundry treatment compositions comprising the beads of the invention and to the use of said beads to slowly release benefit agents.

BACKGROUND OF THE INVENTION

[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] 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. The ratio of D-mannuronate (M) to L-guluronate (G) residues present in the alginate is known as the M:G ratio.

[0004] EP 1 632 560 A1 (P&G) disclose microcapsules for use in a liquid detergent composition. The microcapsules have a core and a polyanion-polycation complex shell wherein the polyanion is capable of gelling in the presence of calcium. The shell acts as a membrane and protects the core, or actives contained in the core from the surrounding medium. The preferred polyanion is alginate having a M:G ratio of at least 1:1; higher M ratios (such as 1.1:1, and 2:1) being more preferred.

[0005] WO 00/46337 (Quest International B.V.) 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. The active materials are substantively insoluble in water and/or sufficiently large (having a molecular weight of at least 5000) to be retained by the alginate.

[0006] WO97/14780 discloses encapsulated bleach particles comprising a galled polymer coating, such as an alginate.

[0007] Many formulations, especially laundry detergents and conditioners (for example powders and liquids) are usually set up to dispense all of their ingredients into water at the start of the wash/rinse process.

[0008] It is therefore desirable to find a system which allows benefit agents to be slowly released into an aqueous medium or onto another substrate.

[0009] The present invention therefore provides a gelled alginate bead, comprising a benefit agent. The bead provides both slow release and retention beyond the main wash stage process of the benefit agent.

SUMMARY OF THE INVENTION

[0010] In a first aspect, this invention is directed to a gelled alginate bead comprising:-

(a) alginate with a M:G ratio of from 0.1:1 to less than 1:1;
(b) one or more cationic species, preferably a divalent or polyvalent metal cation; and,
(c) one or more benefit agents.

[0011] In a second aspect, this invention is directed to a laundry treatment composition comprising the beads of the invention and at least one further laundry ingredient.

[0012] The laundry treatment composition may be a main wash composition, or a composition used in one or more of the rinse cycles of the laundry process.

[0013] Another aspect of the invention relates to the use of a gelled alginate bead comprising:-

(a) alginate with a M:G ratio of from 0.1:1 to less than 1:1;
(b) one or more cationic species, preferably a divalent or polyvalent metal cation; and,
(c) one or more benefit agents,

[0014] in a process for the slow release of said benefit agent into an aqueous medium, preferably a laundry wash liquor.

[0015] A yet further aspect of the present invention relates to a method of treating fabrics with a wash liquor comprising a fabric benefit agent, said fabric benefit agent provided for by one or more beads of the invention, wherein the fabric

benefit agent is slowly released during the wash process.

[0016] A general process for the formation of the gelled alginate beads comprises the following steps:-

(a) provision of a first solution comprising an admixture of alginate having a M:G ratio of from 0.1:1 to less than 1:1 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.

[0017] An alternative process for the formation of the gelled alginate beads comprises the steps:-

(a) provision of a first solution comprising an admixture of alginate having a M:G ratio of from 0.1:1 to less than 1:1 and one or more benefit agents; and,
(b) forming granules of the alginate:benefit agent matrix.

[0018] The beads of the present invention provide numerous advantages in use. For example, they can be used as a carrier to enable the slow release of benefit agents over a longer period of time. This is particularly useful if the benefit agent offers improved benefits when it is present in a substantial proportion of the wash process (i.e. in the main wash and at least one of the rinse stages). Such benefit agents may be lubricants, mild reducing agents, or sequestrants.

[0019] Another advantage of the present invention is that it allows release of the benefit agent to occur after the laundry process is finished. In this case perfumes, or antimicrobial agents are particularly useful as the benefit agents; the delayed release of perfume is perceived as a consumer plus, as perfume smell thus lasts longer past the laundry process; and the delayed release of an antimicrobial agent may help neutralise the bacteria that cause malodour on clothes.

[0020] A further advantage of the present invention is the provision for the slow release of water soluble benefit agents into the wash liquor.

DETAILED DESCRIPTION OF THE INVENTION

[0021] As used herein, the term "comprising" means including, made up of, composed of, consisting and/or consisting essentially of.

[0022] All percentages quoted are wt. % unless otherwise stated.

[0023] 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/or use are to be understood as modified by the word "about".

[0024] "Slow release" used interchangeably herein with "gradual" or "controlled" release means that the chosen benefit agent is released in a delayed fashion. For example, the concentration of the benefit agent present in an aqueous medium (for example a laundry wash/rinse liquor) is replenished, augmented or otherwise added to automatically, and preferably continually over a certain period of time. Such automatic delayed release of benefit agent is distinct from manual addition of additional benefit agent portions, as this is not an automatic, continual release of benefit agent.

[0025] Preferably, when the bead is added to an aqueous medium, the benefit agent comprised therein is continually released over a period of time until total release of benefit agent is achieved.

[0026] Preferably, when used in a laundry wash process, the alginate bead will either:-

a) release all of the benefit agent at a constant rate over the length of the entirety of the wash process, or,
b) release some of the benefit agent at a constant rate over the length of the entire wash process, retaining some of the benefit agent to be released during storage/wear.

[0027] The term "gelled" used herein, is understood to mean that the anionic alginate species has formed a cross-linked network with the cationic species.

Gelled Alginate Beads

[0028] The invention provides gelled alginate beads. The shape of the beads comes will naturally arise from the chosen process of manufacture. However, the beads are generally and preferably in a spherical form.

[0029] The gelled alginate beads can be thought of as a cross-linked alginate/cation matrix network encapsulating one or more benefit agents.

[0030] Preferably the gelled alginate beads are classed as 'matrix' encapsulates, and preferably do not take the form of a core/shell encapsulate whereby the core contains the benefit agent which is surrounded by a protective wall or barrier material.

[0031] The gelled alginate beads can be prepared via several routes. Examples of these routes include:-

1. Diffusion setting, neutral pH: Sodium alginate and/or alginic acid is mixed in a suitable solvent, for example water. The gelled matrix is formed by contacting the solution with another solution containing a divalent or polyvalent metal ion, preferably calcium.

2. Diffusion setting, acid pH: a solution of alginate, benefit agent(s) and a calcium salt which is insoluble at neutral pH is prepared. On contact with an acid solution, the calcium salt is solubilised and reacts with the alginate to form the gel.

3. Internal setting, neutral and acid pH: a solution of alginate, benefit agent(s) and a slowly soluble calcium salt is prepared along with a suitable calcium sequestrant (such as the phosphate or citrate). The sequestrant binds free calcium and prevents pre-gelation during mixing and before it is cast into the desired shape.

4. Setting after heat treatment: the alginate, benefit agent(s), calcium salt and sequestrant are dissolved in a suitable solvent and kept hot. The elevated temperature counteracts the gelation because of the thermal motion of the alginate chains. The gelation begins on cooling.

Cationic Species

[0032] The cationic species form the gelled cross-linked matrix with the alginate. The cationic species may be any cationic species capable of forming a gelled network with alginate. However, metal cations are preferred. Preferred cationic species are those that arise in solution from divalent or polyvalent metal salts. In a preferred embodiment, the cationic species is calcium in the salt form of calcium chloride.

Alginate

[0033] "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.

[0034] 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).*

[0035] The M:G ratio of the alginate used in the present invention is 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 contain a greater number of G residues than M residues. The M:G ratio is preferably 0.1:1 to 0.8:1, more preferably from 0.2:1 to 0.8:1. Certain embodiments of the beads of the present invention comprises 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.*

[0036] The gelled alginate beads comprise alginate with a M:G as defined above. Preferably all of the alginate present in the bead has the aforementioned M:G ratios.

[0037] 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.

[0038] Conveniently, the alginate is used in the form of a sodium salt.

[0039] Suitable alginates with the desired 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.

Benefit Agents

[0040] The beads of the invention comprise a benefit agent. The beads described herein can be used to deliver water-soluble and water-insoluble benefit agents or combinations thereof.

[0041] In one embodiment of the invention, the benefit agent is water soluble. By water soluble, is meant that the benefit agent dissolves in water to an extent of at least 90% by weight in water at 25°C. The beads of the present invention are particularly advantageous for delayed release of benefit agents that are highly water soluble.

[0042] The inclusion level of the benefit agent(s) in the beads is dependant on the amount that is required to achieve the benefit required, the release profile of the agent(s) and the calcium level.

[0043] In the case of benefit agents such as perfumes, fluorescent whitening agents or shading dyes (which are

effective at low levels), the inclusion level would be between 0.00001g and 0.2g per gram of alginate (0.001% to 20% by weight).

[0044] For other benefit agents such as mild reducing agents and sequestrants, the inclusion level could be as high as 0.6g per gram of alginate (60% by weight).

[0045] The benefit agent preferably has a molecular weight below 5000 Daltons, more preferably below 4000 Daltons.

[0046] Any benefit agent is applicable to the present invention. However, preferably the benefit agent is a fabric benefit agent, for laundry purposes.

[0047] Preferably the fabric benefit agent is selected from the group consisting of:- chlorine/oxygen scavengers, antioxidants, 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, or crystal growth inhibitors. The fabric benefit agent may also be a mixture of two or more of the aforementioned benefit agents.

[0048] Most preferably the fabric benefit agent is selected from the group consisting of:- mild reducing agents, sequestrants, perfumes, fluorescent whitening agents, shading dyes, antimicrobial agents or mixtures thereof.

[0049] The term "mild reducing agent" refers to one with a redox potential of between 0 and -800mV in reference to a normal hydrogen electrode.

[0050] Details of the normal hydrogen electrode can be found in: "Encyclopaedia of Analytical Chemistry: Applications, Theory & Instrumentation", R.A. Meyers, 2000 Vol.2 pp 1258-1259 (Published by John Wiley & Sons, ISBN 0471976709).

[0051] A list of redox potentials measured using this technique can be found in the "CRC Handbook of Chemistry and Physics", 86th Edition pp 8.20 - 8.29 (Published by CRC, ISBN 0849304865). Sodium thiosulphate, a preferred reducing agent is listed at -571mV.

[0052] Sequestrants useful as benefit agents in the current invention include: ethylenediaminedisuccinate ("Octaquest (Trade Mark) E30", Octel Performance Chemicals), tetrasodium iminidisuccinate ("Baypure (Trade Mark) CX", Bayer), ethylenediaminetetra(methylene phosphonate ("Dequest (Trade Mark) 2047", Solutia), tetrasodium etidronate ("Turpinal (Trade Mark) 4NP", Solutia). Preferably the sequestrant is ethylenediaminedisuccinate.

[0053] An alternative embodiment includes both sequestrant and mild reducing agent as benefit agents in the bead. For this embodiment, preferably the sequestrant and reducing agent are present in the alginate matrix in equal proportions.

[0054] The perfume, if present, preferably has a molecular weight of from 50 to 500 Daltons.

[0055] The perfume suitably has a boiling point of from 30 to 500°C.

[0056] The beads may optionally further comprise a coloured material if required for aesthetic purposes.

Bead Size

[0057] The size of the beads, measured by the diameter of the beads is from 0.005 to 10mm.

[0058] The beads may be in a dried state or can be in a swollen state. By a swollen state is meant fully hydrated, for example when they are subjected to a liquid, generally water in laundry processes. The bead sizes disclosed herein can apply to beads in a dry state or in a swollen state.

[0059] The bead size can by varied easily in the chosen process of manufacture. For example, in the process described herein, the diameter of the tube that the alginate-benefit agent mixture is passed through can be varied to produce larger or smaller droplets as required.

[0060] In one embodiment of the invention, related to fabric benefit agents, very small bead diameters are preferred. Such bead diameters are in the range of from 0.005 to 0.2mm, preferably from 0.01 to 0.15mm, more preferably from 0.025 to 0.1mm. Without wishing to be bound by any theory, these beads are designed to be small enough to deposit onto a fabric garment, with the fibres present in the fabric garment acting as a fishing net which scoops up the small beads. The small beads then can slowly release the fabric benefit agent after the laundering process (i.e. during storage or wear of the fabric). Fabric benefit agents particularly useful in this system are fragrances (including perfume and perfume mixtures) and anti-microbial materials.

[0061] Alternatively, the beads of the invention may have larger diameters, for example, in the range of from 0.2mm to 10mm. In such an embodiment, preferably the beads have a diameter in the range of from 0.2 to 5mm, more preferably from 0.3 to 3mm.

Form of the Invention

[0062] Laundry treatment composition is herein described to include main wash and rinse products. Preferably the laundry treatment compositions are main wash laundry detergent compositions. Alternatively, they are rinse only compositions, for example rinse conditioners.

[0063] If the laundry treatment composition is to be used in the main wash cycle, i.e. as a laundry detergent composition,

then it 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. In such cases, the laundry treatment composition will comprise one or more detersive surfactants.

[0064] Alternatively, the laundry treatment composition may take the form of a rinse added product, for example, a rinse conditioner. In another embodiment, the beads incorporated within the laundry treatment composition are of a large enough size (for example from 0.2mm to 10mm) to be retained in the drum of the washing machine between either the main wash-rinse cycle step or rinse-rinse cycle steps, depending on at what stage the laundry composition is added.

[0065] The alginate beads may be incorporated into an existing product as an adjunct.

[0066] Typical dosage levels of the gelled alginate beads in a laundry wash or rinse liquor is from 0.01 to 3.0g/l.

Laundry Treatment Composition Ingredients

[0067] The gelled alginate beads of the invention will generally be used in conjunction with a textile compatible carrier in a laundry treatment composition.

[0068] The textile compatible carrier may also provide benefits in addition to those provided by the gelled alginate beads, e.g. softening, cleaning etc. The carrier may be a detergent-active compound or a textile softener or conditioning compound or other suitable detergent or textile treatment agent. Many of these fall within the more general definition 'surfactant' as used herein. The surfactant may comprise the entire carrier or other, non-surfactant carrier materials may be present.

[0069] In a washing process, as part of a conventional textile washing product, such as a detergent composition, the textile-compatible carrier will typically be a detergent-active compound. Whereas, if the textile treatment product is a rinse conditioner, the textile-compatible carrier will be a textile softening and/or conditioning compound. These are described in further detail below.

[0070] Liquid compositions may also include an agent which produces a pearlescent appearance, e.g. an organic pearlising compound such as ethylene glycol distearate, or inorganic pearlising pigments such as microfine mica or titanium dioxide (TiO_2) coated mica. Liquid compositions may be in the form of emulsions or emulsion precursors thereof.

Detergent Active Compounds

[0071] If the composition of the present invention is itself in the form of a detergent composition, the textile-compatible carrier may be chosen from soap and non-soap anionic, cationic, nonionic, amphoteric and zwitterionic detergent active compounds, and mixtures thereof.

[0072] Many suitable detergent active compounds are available and are fully described in the literature, for example, in "Surface-Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch.

[0073] The preferred textile-compatible carriers that can be used are soaps and synthetic non-soap anionic and nonionic compounds.

[0074] Anionic surfactants are well-known to those skilled in the art. Examples include alkylbenzene sulphonates, particularly linear alkylbenzene sulphonates having an alkyl chain length of C_8-C_{15}; primary and secondary alkylsulphates, particularly C_8-C_{15} primary alkyl sulphates; alkyl ether sulphates; olefin sulphonates; alkyl xylene sulphonates; dialkyl sulphosuccinates; and fatty acid ester sulphonates. Sodium salts are generally preferred.

[0075] Nonionic surfactants that may be used include the primary and secondary alcohol ethoxylates, especially the C_6-C_{20} aliphatic alcohols ethoxylated with an average of from 1 to 20 moles of ethylene oxide per mole of alcohol, and more especially the C_{10}-C_{15} primary and secondary aliphatic alcohols ethoxylated with an average of from 1 to 10 moles of ethylene oxide per mole of alcohol. Non-ethoxylated nonionic surfactants include alkylpolyglycosides, glycerol monoethers, and polyhydroxyamides (glucamide).

[0076] Cationic surfactants that may be used include quaternary ammonium salts of the general formula $R_1R_2R_3R_4N^+X^-$ wherein the R groups are independently hydrocarbyl chains of C_1-C_{22} length, typically alkyl, hydroxyalkyl or ethoxylated alkyl groups, and X is a solubilising cation (for example, compounds in which R_1 is a C_8-C_{22} alkyl group, preferably a C_8-C_{10} or C_{12}-C_{14} alkyl group, R_2 is a methyl group, and R_3 and R_4, which may be the same or different, are methyl or hydroxyethyl groups); and cationic esters (for example, choline esters) and pyridinium salts.

[0077] The total quantity of detergent surfactant in the composition is suitably from 0.1 to 60 wt% e.g. 0.5-55 wt%, such as 5-50wt%.

[0078] Preferably, the quantity of anionic surfactant (when present) is in the range of from 1 to 50% by weight of the total composition. More preferably, the quantity of anionic surfactant is in the range of from 3 to 35% by weight, e.g. 5 to 30% by weight.

[0079] Preferably, the quantity of nonionic surfactant (when present) is in the range of from 2 to 25% by weight, more preferably from 5 to 20% by weight.

[0080] Amphoteric surfactants may also be used, for example amine oxides or betaines.

Builders

[0081] The laundry detergent compositions may suitably contain from 10 to 70%, preferably from 15 to 70% by weight, of detergency builder. Preferably, the quantity of builder is in the range of from 15 to 50% by weight.

[0082] The detergent composition may contain as builder a crystalline aluminosilicate, preferably an alkali metal aluminosilicate, more preferably a sodium aluminosilicate.

[0083] The aluminosilicate may generally be incorporated in amounts of from 10 to 70% by weight (anhydrous basis), preferably from 25 to 50%. Aluminosilicates are materials having the general formula:

$$0.8\text{-}1.5\ M_{20}.\ Al_2O_3.\ 0.8\text{-}6\ SiO_2$$

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.

[0084] Alternatively, or additionally to the aluminosilicate builders, phosphate builders may be used.

Textile Softening and/or Conditioner Compounds:

[0085] If the laundry treatment composition is in the form of a textile conditioner composition, the textile-compatible carrier will be a textile softening and/or conditioning compound (hereinafter referred to as "textile softening compound"), which may be a cationic or nonionic compound. The softening and/or conditioning compounds may be water insoluble quaternary ammonium compounds. The compounds may be present in amounts of up to 8% by weight (based on the total amount of the composition) in which case the compositions are considered dilute, or at levels from 8% to about 50% by weight, in which case the compositions are considered concentrates.

[0086] Compositions suitable for delivery during the rinse cycle may also be delivered to the textile in the tumble dryer if used in a suitable form. Thus, another product form is a composition (for example, a paste) suitable for coating onto, and delivery from, a substrate e.g. a flexible sheet or sponge or a suitable dispenser during a tumble dryer cycle.

[0087] Suitable cationic textile softening compounds are substantially water-insoluble quaternary ammonium materials comprising a single alkyl or alkenyl long chain having an average chain length greater than or equal to C_{20}. More preferably, softening compounds comprise a polar head group and two alkyl or alkenyl chains having an average chain length greater than or equal to C_{14}. Preferably the textile softening compounds have two, long-chain, alkyl or alkenyl chains each having an average chain length greater than or equal to C_{16}.

[0088] Most preferably at least 50% of the long chain alkyl or alkenyl groups have a chain length of C_{18} or above. It is preferred if the long chain alkyl or alkenyl groups of the textile softening compound are predominantly linear. Quaternary ammonium compounds having two long-chain aliphatic groups, for example, distearyldimethyl ammonium chloride and di(hardened tallow alkyl) dimethyl ammonium chloride, are widely used in commercially available rinse conditioner compositions. Other examples of these cationic compounds are to be found in "Surface-Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch. Any of the conventional types of such compounds may be used in the compositions of the present invention.

[0089] The textile softening compounds are preferably compounds that provide excellent softening, and are characterised by a chain melting Lβ to Lα transition temperature greater than 25°C, preferably greater than 35°C, most preferably greater than 45°C. This Lβ to Lα transition can be measured by DSC as defined in "Handbook of Lipid Bilayers", D Marsh, CRC Press, Boca Raton, Florida, 1990 (pages 137 and 337).

[0090] Substantially water-insoluble textile softening compounds are defined as textile softening compounds having a solubility of less than 1×10^{-3} wt. % in demineralised water at 20°C. Preferably the textile softening compounds have a solubility of less than 1×10^{-4} wt. %, more preferably less than 1×10^{-3} to 1×10^{-6} wt . %.

[0091] Especially preferred are cationic textile softening compounds that are water-insoluble quaternary ammonium materials having two $C_{12\text{-}22}$ alkyl or alkenyl groups connected to the molecule via at least one ester link, preferably two ester links. Di(tallowoxyloxyethyl) dimethyl ammonium chloride and/or its hardened tallow analogue are especially preferred of the compounds of this type. Other preferred materials include 1,2-bis(hardened tallowoyloxy)-3-trimethylammonium propane chloride. Their methods of preparation are, for example, described in US 4 137 180 (Lever Brothers Co). Preferably these materials comprise small amounts of the corresponding monoester as described in US 4 137 180, for example, 1-hardened tallowoyloxy-2-hydroxy-3-trimethylammonium propane chloride.

[0092] Other useful cationic softening agents are alkyl pyridinium salts and substituted imidazoline species. Also useful are primary, secondary and tertiary amines and the condensation products of fatty acids with alkylpolyamines.

[0093] The compositions may alternatively or additionally contain water-soluble cationic textile softeners, as described in GB 2 039 556B (Unilever).

[0094] The compositions may comprise a cationic textile softening compound and an oil, for example as disclosed in EP-A-0829531.

[0095] The compositions may alternatively or additionally contain nonionic textile softening agents such as lanolin and derivatives thereof.

[0096] Lecithins are also suitable softening compounds.

[0097] Nonionic softeners include Lβ phase forming sugar esters (as described in M Hato et al Langmuir 12, 1659, 1666, (1996)) and related materials such as glycerol monostearate or sorbitan esters. Often these materials are used in conjunction with cationic materials to assist deposition (see, for example, GB 2 202 244). Silicones are used in a similar way as a co-softener with a cationic softener in rinse treatments (see, for example, GB 1 549 180).

[0098] The compositions may also suitably contain a nonionic stabilising agent. Suitable nonionic stabilising agents are linear C_8 to C_{22} alcohols alkoxylated with 10 to 20 moles of alkylene oxide, C_{10} to C_{20} alcohols, or mixtures thereof.

[0099] Advantageously the nonionic stabilising agent is a linear C_8 to C_{22} alcohol alkoxylated with 10 to 20 moles of alkylene oxide. Preferably, the level of nonionic stabiliser is within the range from 0.1 to 10% by weight, more preferably from 0.5 to 5% by weight, most preferably from 1 to 4% by weight. The mole ratio of the quaternary ammonium compound and/or other cationic softening agent to the nonionic stabilising agent is suitably within the range from 40:1 to about 1:1, preferably within the range from 18:1 to about 3:1.

[0100] The composition can also contain fatty acids, for example C_8 to C_{24} alkyl or alkenyl monocarboxylic acids or polymers thereof. Preferably saturated fatty acids are used, in particular, hardened tallow C_{16} to C_{18} fatty acids. Preferably the fatty acid is non-saponified, more preferably the fatty acid is free, for example oleic acid, lauric acid or tallow fatty acid. The level of fatty acid material is preferably more than 0.1% by weight, more preferably more than 0.2% by weight. Concentrated compositions may comprise from 0.5 to 20% by weight of fatty acid, more preferably 1% to 10% by weight. The weight ratio of quaternary ammonium material or other cationic softening agent to fatty acid material is preferably from 10:1 to 1:10.

Optional Ingredients

[0101] Compositions according to the invention may comprise soil release polymers such as block copolymers of polyethylene oxide and terephthalate.

[0102] Other optional ingredients include emulsifiers, electrolytes (for example, sodium chloride or calcium chloride) preferably in the range from 0.01 to 5% by weight, pH buffering agents, and perfumes (preferably from 0.1 to 5% by weight) .

[0103] Further optional ingredients include non-aqueous solvents, perfume carriers, colourants, hydrotropes, anti-foaming agents, enzymes and opacifiers.

[0104] Suitable enzymes include proteases, amylases, lipases, cellulases, peroxidases and mixtures thereof.

[0105] In addition, compositions may comprise one or more of anti-shrinking agents, anti-wrinkle agents, anti-spotting agents, germicides, fungicides, antioxidants, UV absorbers (sunscreens), dye fixatives, anti-corrosion agents, drape imparting agents, antistatic agents and ironing aids. The lists of optional components are not intended to be exhaustive.

[0106] The following non-limiting examples will more fully illustrate specific embodiments of this invention. All parts, percentages and proportions referred to herein and in the appended claims are by weight unless otherwise illustrated. Physical test methods are described below.

EXAMPLES

[0107] Gelled alginate beads were prepared as follows:

[0108] The alginate (4.5g) and benefit agent (sodium thiosulphate pentahydrate, 4.5g) were dissolved in demin water (200ml) and mixed until homogeneous. The solution was then pumped via narrow bore (0.6mm internal diameter) tubing and allowed to drip into a solution of calcium chloride (3.5g/l, 500ml) from a height of approximately 20cm with slow continuous stirring via a magnetic stirrer.

[0109] When all the alginate solution has been pumped into the calcium chloride solution, the gelled alginate beads were filtered through a 0.5mm sieve and dried between multiple sheets of absorbent paper. The beads were then transferred to a large flat glass dish and dried at 70°C until all the beads had collapsed down to form irregular beads of <1mm.

[0110] Gelled alginate beads comprising sodium thiosulphate (a mild reducing agent known in laundry) were prepared as follows:

Example 1 - Baseline alginate beads

[0111] 4.5g of Manugel™ GMB was dissolved in 200ml demin water and dripped into 500ml of calcium chloride (3.5g/l).

The beads were then filtered and dried. The final weight allowed the amount of calcium incorporated into the beads to be calculated. From this the level of thiosulphate could also be calculated for examples 2 and 3.

Mass of dried beads = 4.75g
Composition = 94.7% alginate, 5.3% calcium.

Example 2 - Comparative example

[0112] 4.5g of Manucol™ DH (sodium alginate, M:G ratio 2.33 ex. International Speciality Products) was mixed with 4.5g sodium thiosulphate pentahydrate and dripped into 3.5g/l calcium chloride solution.

Mass of beads after drying: 6.17g
Composition = 72.9% alginate, 4.1% calcium, 23.6% sodium thiosulphate.

Example 3 - according to the invention

[0113] As example 1, but Manucol™ DH was replaced with Manugel™ GMB, M:G ratio 0.43.

Mass of beads after drying: 6.22g
Composition = 72.3% alginate, 4.0% calcium, 23.7% sodium thiosulphate.

Thiosulphate release of examples 2 and 3

[0114] Iodiometric spectroscopy was used to measure the rate of release of thiosulphate over time.

[0115] To determine the release profile, 2.5ml of 0.05N iodine was diluted into 197.5ml of demineralised water or surfactant solution (1g/l of linear alkyl benzene sulphonate + 1g/l Neodol 25/7 - 7EO C_{12}/C_{15} linear alcohol ethoxylate). The solution was pumped through a flowcell in the spectrometer and the absorption at 453nm recorded. The required quantity of alginate beads were then added with constant stirring and the decrease in absorption measured over a period of 1 hour. Table 1 shows the difference in release rate of the two granules:

Table 1 Showing the percentage of thiosulphate released (by measuring absorbance) from the beads during a 1 hr process

Time (min)	Abs. @ 45nm for Manugel DH (example 2)	% Thiosulphate released	Abs. @ 45nm for Manugel GMB (example 3)	% Thiosulphate released
0	0.4671	0.00	0.4671	0.00
5	0.0669	85.68	0.3928	15.90
10	0.0411	91.20	0.3169	32.16
15	0.0359	92.31	0.2498	46.51
20	0.0349	92.53	0.1901	59.30
25	0.0358	92.35	0.1385	70.35
30	0.0354	92.42	0.0951	79.63
35	0.0354	92.42	0.0599	87.18
40	0.0366	92.17	0.0340	92.72
45	0.0358	92.34	0.0165	96.47
50	0.0360	92.29	0.0041	99.13
55	0.0349	92.52	0.0004	99.92
60	0.0348	92.56	0.0003	99.95

[0116] The alginate bead based on the high M:G ratio alginate (Manugel (Trade Mark) DH) shows 86% release within 5 minutes and 92.5% release after 60 minutes. The alginate bead according to the invention based on a low M:G ratio

shows a desired delayed release profile.

[0117] The experiment also shows that beads according to the invention display an additional advantage of near 100% release occurring within the time period. This is advantageous for certain processes when residue is not desired on the laundered fabrics.

Table 2 Showing the percentage of thiosulphate released (by measuring absorbance) from the example 3 beads during a 1 hr process into water and surfactant solution.

Time (min)	Release into water	% Thiosulphate released	Release into surfactant solution	% Thiosulphate released
0	0.4671	0.00	0.4671	0.00
5	0.3928	15.90	0.3888	16.76
10	0.3169	32.16	0.3025	35.24
15	0.2498	46.51	0.2191	53.10
20	0.1901	59.30	0.1490	68.11
25	0.1385	70.35	0.0945	79.78
30	0.0951	79.63	0.0570	87.80
35	0.0599	87.18	0.0326	93.03
40	0.0340	92.72	0.0175	96.26
45	0.0165	96.47	0.0089	98.10
50	0.0041	99.13	0.0046	99.02
55	0.0004	99.92	0.0020	99.57
60	0.0003	99.95	0.0004	99.92

Example 4 - Cross-wash Release in a front-loading washing machine

[0118] In order to verify the ability of the alginate granules to (a) be retained in the machine after the main wash and (b) to release the benefit agent in the rinse stages, gelled alginate beads as prepared in example 3 were used in the following experiment.

[0119] Three loads were prepared comprising equal amounts of undyed non-fluorescent woven and knitted cotton (50x50cm in size, 1.25kg of each fabric type).

[0120] The loads were washed in computer-controlled Miele (Trade Mark) front loading washing machines using the following wash program:

1. Fill, 15 litres demin water
2. Wash, 35 mins @ 40°C
3. Flood fill up to 21 litres
4. Drain
5. Fill, 21 litres demin water
6. Rinse, 120 seconds
7. Drain
8. Spin, 60 seconds @ 90rpm
9. Repeat stages 5-8 a further 3 times
10. Spin, 120 seconds @ 400rpm
11. Spin, 300 seconds @ 1200rpm
12. Spin, 60 seconds @ 90rpm

[0121] Samples of the liquor were removed from the machine prior to each drain stage so that the level of sodium thiosulphate could be measured.

[0122] Powder used - 110g of Persil™ Colour (commercial bleach-free washing powder as available commercially).

[0123] Wash 2 had 0.2g of sodium thiosulphate pentahydrate added to the main wash and to each of the four rinse stages during the fill process.

[0124] Wash 3 had 3.3g of gelled alginate beads added into the main wash (expected to deliver 1g of sodium thiosulphate pentahydrate across the wash).

[0125] Upon completion of the experiment, the liquor samples were allowed to cool to room temperature. The pH was measured and then adjusted to pH 7 with 1.0N hydrochloric acid. The residual powder was then removed from the samples by filtration through a 0.45μm cellulose filter.

[0126] 5ml of each filtered sample was then added to 10ml of iodine solution (4ml 0.05M iodine in 1 litre demin water) in a 50mm pathlength cell and the absorption at 453nm measured.

[0127] The absorption was then used to calculate the amount of thiosulphate present in the liquor.

[0128] The results obtained were:

	Alginate granule	Manual addition*	Mainwash only*
Main wash	0.5040g	0.2000g	1.0000g
1st rinse	0.1000g	0.2167g	0.0832g
2nd rinse	0.1430g	0.2181g	0.0069g
3rd rinse	0.1100g	0.2182g	0.0006g
4th rinse	0.1120g	0.2182g	0.0001g

[0129] In the case of the alginate granules, the total released is 0.969g. The figures for mainwash addition only are calculated based on carryover from one stage to the next using an experimentally obtained water retention figure of 70% (thus a 2.5kg load will retain 1.75kg of liquor at the end of each stage).

[0130] The presence of thiosulphate in all the rinse stages indicates that the gelled alginate beads have been retained within the machine during the wash process at a level that cannot be accounted for by carryover of wash liquor from one rinse stage to the next.

Claims

1. A gelled alginate bead comprising:-

   (a) alginate with a D-mannuronate (M) : L-guluronate (G) ratio of from 0.1:1 to less than 1 : 1;
   (b) one or more cationic species, preferably a divalent or polyvalent metal cation; and,
   (c) one or more benefit agents.

2. A bead according to claim 1, wherein the alginate has a M:G ratio of from 0.1:1 to 0.8:1, preferably from 0.2:1 to 0.8:1.

3. A bead according to claim 1 or claim 2, wherein the cationic species is a divalent or polyvalent metal cation.

4. A bead according to claim 3, wherein the cationic species is a divalent metal cation, preferably calcium.

5. A bead according to claim 4, wherein the benefit agent is a fabric benefit agent.

6. A bead according to claim 5, wherein the fabric benefit is selected from the group consisting of chlorine/oxygen scavengers, antioxidants, 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.

7. A bead according to claim 5, wherein the fabric benefit is selected from the group consisting of: mild reducing agents, sequestrants, perfumes, fluorescent whitening agents, shading dyes, anti-microbial agents or mixtures thereof.

8. A bead according to any preceding claim, wherein the benefit agent is water soluble.

9. A bead according to any one of the preceding claims, wherein the bead has a diameter of from 0.005 to 10mm when swollen.

10. A bead according to claim 9, wherein the bead has a diameter of from 0.005 to 0.2mm when swollen.

11. A laundry treatment composition comprising the beads of any one of claims 1 to 10 and at least one further laundry ingredient, preferably a textile compatible carrier.

12. Use of a gelled alginate bead comprising:-

(a) alginate with a M:G ratio of from 0.1:1 to less than 1:1;
(b) one or more cationic species, preferably a monovalent or polyvalent metal cation; and,
(c) one or more benefit agents,

in a process for the slow release of said benefit agent into an aqueous medium, preferably a laundry wash liquor.

13. A method of treating fabrics with a wash liquor comprising a fabric benefit agent, said fabric benefit agent provided by one or more beads of claims 1 to 10, wherein the fabric benefit agent is slowly released during the wash process.

Patentansprüche

1. Perle aus geliertem Alginat, umfassend:

(a) Alginat mit einem D-Mannuronat (M):L-Guluronat (G)-Verhältnis von 0,1:1 bis kleiner als 1:1;
(b) eine oder mehrere kationische Spezies, vorzugsweise ein zweiwertiges oder mehrwertiges Metallkation, und
(c) ein oder mehrere Mittel mit günstigen Eigenschaften.

2. Perle nach Anspruch 1, wobei das Alginat ein M:G-Verhältnis von 0,1:1 bis 0,8:1, vorzugsweise von 0,2:1 bis 0,8:1 hat.

3. Perle nach Anspruch 1 oder Anspruch 2, wobei die kationische Spezies ein zweiwertiges oder mehrwertiges Metallkation ist.

4. Perle nach Anspruch 3, wobei die kationische Spezies ein zweiwertiges Metallkation, vorzugsweise Calcium, ist.

5. Perle nach Anspruch 4, wobei das Mittel mit günstigen Eigenschaften ein Mittel mit für Gewebe günstigen Eigenschaften ist.

6. Perle nach Anspruch 5, wobei das Mittel mit für Gewebe günstigen Eigenschaften ausgewählt ist aus der Gruppe, bestehend aus Chlor/Sauerstoff-Fängern, Antioxidantien, Sequestriermitteln, Parfüms, antimikrobiellen Mitteln, antibakteriellen Mitteln, antifungalen Mitteln, Gleitmitteln, UV-Absorptionsmitteln, Farbtönungsmitteln, fluoreszierenden Weißtönern, Dispergiermitteln, Mitteln gegen Wiederabscheidung, Schmutzentfernungsmitteln, Enzymen zur Entfernung von Fusseln oder Kügelchen oder zur Verhinderung von Flecken, Farbstoffübertragungs-Inhibitoren, Farbstoffsequestriermitteln, Farbstofffixierungsmitteln, Weichmachern, Inhibitoren des Kristallwachstums oder Gemischen davon.

7. Perle nach Anspruch 5, wobei das Mittel mit für Gewebe günstigen Eigenschaften ausgewählt ist aus der Gruppe, bestehend aus: milden Reduktionsmitteln, Sequestriermitteln, Parfüms, fluoreszierenden Weißtönern, Tönungsfarbstoffen, antimikrobiellen Mitteln oder Gemischen davon.

8. Perle nach einem vorangehenden Anspruch, wobei das Mittel mit günstigen Eigenschaften wasserlöslich ist.

9. Perle nach einem der vorangehenden Ansprüche, wobei die Perle einen Durchmesser von 0,005 bis 10 mm hat, wenn sie gequollen ist.

10. Perle nach Anspruch 9, wobei die Perle einen Durchmesser von 0,005 bis 0,2 mm hat, wenn sie gequollen ist.

11. Wäschebehandlungs-Zusammensetzung, umfassend die Perlen nach einem der Ansprüche 1 bis 10 und wenigstens ein weiteres Wasch-Ingrediens, vorzugsweise einen mit Textilien kompatiblen Träger.

12. Verwendung einer Perle aus geliertem Alginat, umfassend:

(a) Alginat mit einem M:G-Verhältnis von 0,1:1 bis kleiner als 1:1;
(b) eine oder mehrere kationische Spezies, vorzugsweise ein einwertiges oder mehrwertiges Metallkation, und
(b) ein oder mehrere Mittel mit günstigen Eigenschaften,

in einem Verfahren für die langsame Freisetzung des Mittels mit günstigen Eigenschaften in ein wässriges Medium, vorzugsweise eine Wäschewaschlauge.

13. Verfahren zur Behandlung von Geweben mit einer Waschlauge, die ein Mittel mit für Gewebe günstigen Eigenschaften umfasst, wobei das Mittel mit für Gewebe günstigen Eigenschaften durch eine oder mehrere Perlen nach den Ansprüchen 1 bis 10 bereitgestellt wird, wobei das Mittel mit günstigen Eigenschaften für Gewebe während des Waschprozesses langsam freigesetzt wird.

Revendications

1. Bille d'alginate gélifiée, comprenant :

(a) de l'alginate avec un rapport D-mannuronate (M) : L-guluronate (G) de 0,1:1 à moins de 1:1 ;
(b) une ou plusieurs espèces cationiques, de préférence un cation de métal divalent ou polyvalent ; et
(c) un ou plusieurs agents bénéfiques.

2. Bille selon la revendication 1, dans laquelle l'alginate a un rapport M:G de 0,1:1 à 0,8:1, de préférence de 0,2:1 à 0,8:1.

3. Bille selon la revendication 1 ou la revendication 2, dans laquelle l'espèce cationique est un cation métallique divalent ou polyvalent.

4. Bille selon la revendication 3, dans laquelle l'espèce cationique est un cation métallique divalent, de préférence le calcium.

5. Bille selon la revendication 4, dans laquelle l'agent bénéfique est un agent bénéfique pour tissu.

6. Bille selon la revendication 5, dans laquelle l'agent bénéfique pour tissu est choisi dans le groupe constitué par les fixateurs de chlore/ oxygène, les antioxydants, les agents séquestrants, les parfums, les agents antimicrobiens, les agents antibactériens, les agents antifongiques, les lubrifiants, les agents anti-UV, les teintes de nuançage, les agents blanchissants fluorescents, les dispersants, les agents antiredéposition, les agents anti-salissures, les enzymes pour éliminer la poussière ou les bouloches ou empêcher le dégorgement, les inhibiteurs de transfert de teinte, des séquestrants de teinte, des fixateurs de teinte, les adoucissants, les inhibiteurs de croissance cristalline, ou leurs mélanges.

7. Bille selon la revendication 5, dans laquelle l'agent bénéfique pour tissu est choisi dans le groupe constitué par : les agents réducteurs modérés, les séquestrants, les parfums, les agents blanchissants fluorescents, les teintes de nuançage, les agents antimicrobiens ou leurs mélanges.

8. Bille selon l'une quelconque des revendications précédentes, dans laquelle l'agent bénéfique est soluble dans l'eau.

9. Bille selon l'une quelconque des revendications précédentes, dans laquelle la bille a un diamètre de 0,005 à 10 mm une fois gonflée.

10. Bille selon la revendication 9, dans laquelle la bille a un diamètre de 0,005 à 0,2 mm une fois gonflée.

11. Composition de traitement du linge comprenant les billes selon l'une quelconque des revendications 1 à 10 et au moins un ingrédient supplémentaire pour le linge, de préférence un vecteur compatible avec le textile.

12. Utilisation d'une bille d'alginate gélifiée comprenant :

(a) un alginate avec un rapport M:G de 0,1:1 à moins de 1:1 ;
(b) une ou plusieurs espèces cationiques, de préférence un cation métallique monovalent ou polyvalent ; et
(c) un ou plusieurs agents bénéfiques,

dans un processus pour la libération lente dudit agent bénéfique dans un milieu aqueux, de préférence une lessive pour le lavage du linge.

13. Procédé de traitement de tissus avec une lessive de lavage comprenant un agent bénéfique pour le tissu, ledit agent bénéfique pour le tissu étant formé par une ou plusieurs billes selon les revendications 1 à 10, où l'agent bénéfique pour le tissu est libéré lentement pendant le processus de lavage.

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- EP 1632560 A1, P&G **[0004]**
- WO 0046337 A, Quest International B.V. **[0005]**
- WO 9714780 A **[0006]**
- US 4137180 A **[0094]**
- GB 2039556 B, Unilever **[0096]**
- EP 0829531 A **[0097]**
- GB 2202244 A **[0100]**
- GB 1549180 A **[0100]**

Non-patent literature cited in the description

- **R.A. Meyers.** Encyclopaedia of Analytical Chemistry: Applications, Theory & Instrumentation. John Wiley & Sons, 2000, vol. 2, 1258-1259 **[0053]**
- CRC Handbook of Chemistry and Physics. CRC, 8.20-8.29 **[0054]**
- **D Marsh.** Handbook of Lipid Bilayers. CRC Press, 1990, 137-337 **[0092]**
- **M Hato et al.** *Langmuir,* 1996, vol. 12, 1659, 1666 **[0100]**