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(54) **Title:** POLYMER SHELL MICROCAPSULES WITH DEPOSITION POLYMER(57) **Abstract:** A microcapsule containing a benefit agent inside a polyurea shell characterised in that polyurea has a nonionic poly-saccharide deposition polymer covalently bonded to it. Also a process for making the microcapsule and compositions incorporating the microcapsule.

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POLYMER SHELL MICROCAPSULES WITH DEPOSITION POLYMER**TECHNICAL FIELD**

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This invention relates to polymer shell microcapsules with deposition polymer for the delivery of benefit agents, to their incorporation into consumer products and to a process for making the microcapsules.

BACKGROUND

WO07062833 (Unilever) discloses in example 2 the grafting of a locust bean gum deposition polymer onto a polyurethane capsule using vinyl acetate addition polymerization. Claim 7 mentions polyxyloglucan (also called xyloglucan) as uncharged polysaccharide material and claim 3 mentions melamine formaldehyde as shell material.

WO08145547 (Unilever) discloses a process for attachment of a nonionic deposition polymer, substantive to textiles, to core shell particles. Example 7 forms melamine formaldehyde microcapsules and then attaches a locust bean gum deposition polymer to them using melamine formaldehyde pre-polymer. Example 8 attaches both locust bean gum and xyloglucan nonionic deposition polymers to microcapsules by use of various addition polymers.

WO2012/007438 (Unilever) discloses a benefit agent containing particle comprising a multi layered shell in which the outer shell may be a polyurea (see page 8 line 27) with a deposition polymer exterior to the shell (claim 4 and p28-30). The inner shell is poly methacrylate. Page 36 suggests to add deposition polymer late and, if necessary, with "further isocyanate and co-monomer". Example 1 is polyurethane. The only deposition polymer used is a PET-POET polymer chain post-grafted onto polyurethane with polyurethane (from a condensation reaction).

WO2012/038144 (Unilever) discloses in example 1 the attachment of a Xyloglucan deposition agent to preformed melamine formaldehyde perfume microcapsules by means

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of a pre-polymer solution of further melamine formaldehyde. The perfume deposition in the absence of mannanase enzyme was shown to be the same as locust bean gum. In the presence of mannanase the xyloglucan performed significantly better than the locust bean gum control. In example 3 the deposition agents were attached using vinyl acetate.

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US2014/0142019 (Unilever) discloses a benefit agent delivery particle comprising hydroxypropylcellulose (HPC). The benefit agent delivery particle may further comprise a non-polysaccharide polymer, preferably an aminoplast polymer. The benefit agent delivery particle may comprise a perfume.

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The process for the preparation of the particles is preferably a two-step process in which the first step forms a particle comprising the benefit agent and the second step applies a coating to the capsule which includes the HPC as a deposition polymer. The first step can either be step-growth or addition polymerisation and the second step (i.e. the attachment of the HPC) is preferably addition polymerisation. Suitable classes of monomers for step-growth polymerization are given in the group consisting of the melamine/ urea/ formaldehyde class, the isocyanate/ diol class (preferably the polyurethanes) and polyesters. Preferred are the melamine/urea formaldehyde class and the polyurethanes. Para 73 and 74 teach that the HPC deposition polymer is attached using vinyl acetate and or methyl acrylate.

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Encapsulates (microcapsules) made using formaldehyde suffer from problems with evolution of formaldehyde and a formaldehyde scavenger is employed. This adds to chemical loading and can inhibit formulation flexibility. Lately, melamine formaldehyde, which has for many years been preferred over urea formaldehyde due to its reduced tendency to evolve formaldehyde, has come under pressure for elimination in consumer products due to its potential persistence in the environment. An alternative shell material for perfume microcapsules for delivery of other benefit agents in consumer products is therefore sought. Polyurethane has been proposed as an alternative but the reaction of isocyanates with polyols requires the use of further chemicals to initiate it and they can cause problems if they come into contact with many sensitive benefit agents. Typically a polyurethane capsule has to be finished off with an amine that reacts onto the large

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number of unreacted isocyanate sites in the polyurethane shell. This is a cumbersome procedure and makes these particles expensive to produce even if the initiators are compatible with the benefit agent contents. Addition of a nonionic polysaccharide deposition polymer to such a complex base particle would most likely require the use of
5 addition polymers, yet further complicating the chemistry and adding cost.

It is desirable that the deposition polymer for an alternative shell material is the one already shown to be advantageous for melamine formaldehyde; i.e. a nonionic polysaccharide. To achieve the elimination of melamine formaldehyde from the product
10 the attachment of such a deposition polymer to a non-melamine formaldehyde shell material cannot be achieved using the known pre-polymer route as commonly employed for melamine formaldehyde. The known alternative "addition polymer" route has never found favour outside of the laboratory because it complicates the manufacturing process excessively. It was therefore necessary to find a different shell wall material suitable for
15 use with the advantageous nonionic deposition polymers and to devise a new process to attach those nonionic polysaccharide polymers to that shell wall material.

US 2012/0148644A1 (IFF) describes the synthesis of microcapsules with polyurea shells (para 180) for delivery of perfume as a benefit agent. The polyurea is preferentially
20 formed using interfacial polymerisation of polyisocyanate and diamine. In the examples they disclose that carboxymethyl cellulose may be used to enhance perceived fragrance intensity (para 185). They also disclose adding deposition polymers (at start, during and after capsule formation) but these are cationic (or amphoteric) and not polysaccharide based (para 189). Merquat 100 is a highly charged cationic polymer.

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SUMMARY OF THE INVENTION

According to the present invention there is provided a microcapsule containing a benefit agent inside a polyurea shell characterised in that the polyurea has a nonionic polysaccharide deposition polymer covalently bonded to it. Nonionic deposition polymers are known to provide enhanced deposition onto cellulosic materials for other types of shell material. When attached to polyurea we have surprisingly found that compared to when attached to prior art microcapsules they provide reduced agglomeration of the microcapsules and an ability for the microcapsules to remain better dispersed in surfactant containing products.

Preferably the deposition polymer is selected from the group consisting of mannan, glucan, glucomannan, xyloglucan, hydroxyalkyl cellulose, dextran, galactomannan and mixtures thereof. More preferably the deposition polymer is xyloglucan, galactomannan, dextran or hydroxypropyl cellulose and most preferably it is a xyloglucan or hydroxypropyl cellulose.

Preferred nonionic polysaccharides are those with a molecular weight Mw in excess of 40 kDa.

The weight ratio of deposition polymer to polyurea shell preferably lies in the range 1:500 to 1:2 as this achieves the surprising benefits previously noted. The inventive effect is advantageously obtainable at low levels of grafting of from 1:500 to 1:10, even 1:400 to 1:20, nonionic deposition polymer to polyurea shell.

The microcapsule preferably comprises at least 50 wt%, more preferably over 80 wt% core materials, including the benefit agent, and 1 to 30 wt% polyurea shell. More preferably the shell comprises up to 10 wt% of the microcapsule. The amount of shell is adjusted as known by the person skilled in the art to tune the friability of the microcapsule and to effectively retain its contents. The amount of benefit agent as a wt% of the total is preferably at least 10 wt%, more preferably at least 20 wt%, even more preferably at least 30 wt% and most preferably at least 40 wt% or even at least 50 wt%.

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The deposition polymer level is preferably from 0.1 to 10 wt%, more preferably 0.2 to 5 wt%, based on microcapsule weight.

5 The polyurea may advantageously be formed by the reaction of poly-isocyanate and diamine. The poly functionality of the isocyanate is thought to provide sufficient free isocyanate reaction sites for the covalent bonding to occur easily.

Compositions will preferably include at least 0.01 wt% of the microcapsules. They will typically further include either a surfactant or cationic material.

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Preferably, the microcapsule containing composition is a laundry detergent and the composition further comprises at least 5 wt% anionic surfactant.

15 Alternatively, the microcapsule containing composition is a skin cleansing composition or hair shampoo composition and the composition further comprises at least 2 wt% surfactant.

Alternatively, the microcapsule containing composition is a hair conditioner composition and the composition further comprises at least 1 wt% cationic material.

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Compositions comprising the microcapsules are preferably consumer products and according to consumer preference and to mask the odour from other ingredients the compositions preferably further comprise at least 0.1 wt% perfume in addition to surfactant or cationic material.

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Also according to the present invention there is provided a method of making the microcapsules containing a benefit agent inside a polyurea shell which has a nonionic polysaccharide deposition polymer covalently bonded to it, wherein the nonionic polysaccharide is added at least 15 minutes after commencement of curing of the
30 polyurea.

DETAILED DESCRIPTION OF THE INVENTION**The nonionic polysaccharide deposition polymer**

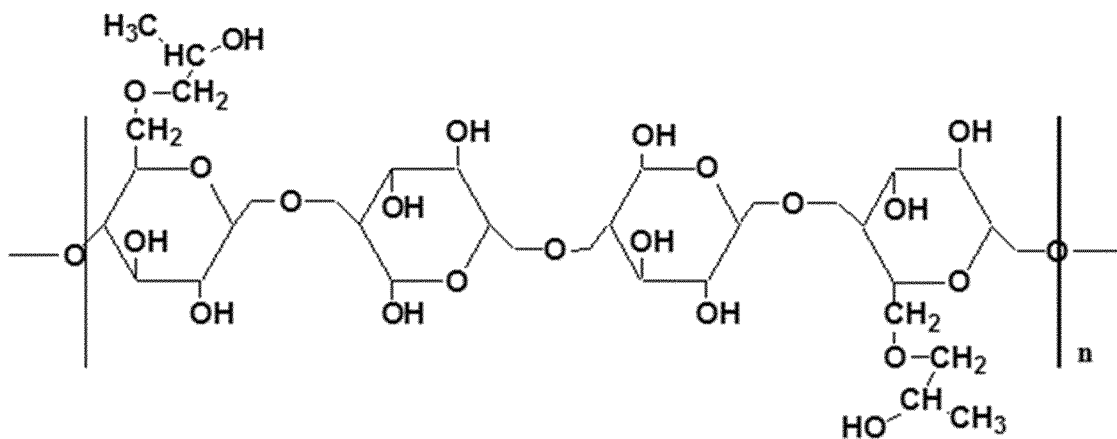
5 Preferred nonionic polysaccharide deposition polymers may be selected from the group consisting of: tamarind gum (preferably consisting of xyloglucan polymers), guar gum, locust bean gum (preferably consisting of galactomannan polymers), and other industrial gums and polymers, which include, but are not limited to, Tara, Fenugreek, Aloe, Chia, Flaxseed, Psyllium seed, quince seed, xanthan, gellan, welan, rhamosan, dextran, curdlan,
10 pullulan, scleroglucan, schizophyllan, chitin, hydroxyalkyl cellulose, arabinan (preferably from sugar beets), de- branched arabinan (preferably from sugar beets), arabinoxylan (preferably from rye and wheat flour), galactan (preferably from lupin and potatoes), pectic galactan (preferably from potatoes), galactomannan (preferably from carob, and including both low and high viscosities), glucomannan, lichenan (preferably from icelandic
15 moss), mannan (preferably from ivory nuts), pachyman, rhamnogalacturonan, acacia gum, agar, alginates, carrageenan, chitosan, clavan, hyaluronic acid, heparin, inulin, cellodextrins, cellulose, cellulose derivatives and mixtures thereof.

Non-hydrolysable nonionic polysaccharides are most preferred. The polysaccharide
20 preferably has a β -1,4-linked backbone. However, dextran which does not have such a backbone, is also preferred.

Preferably the polysaccharide is a cellulose, a cellulose derivative, or another β -1,4-linked polysaccharide having an affinity for cellulose, preferably mannan, glucan, glucomannan,
25 xyloglucan, galactomannan and mixtures thereof. More preferably, the polysaccharide is selected from the group consisting of xyloglucan and hydroxypropyl cellulose. Galactomannan is typically from Locust bean gum and / or guar.

A highly preferred nonionic polysaccharide is Hydroxypropyl Cellulose with a molecular
30 weight in excess of 40 kDa. Hydroxypropyl Cellulose (HPC) has the repeat structure shown in generalised terms below:

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Especially good results may be obtained when the HPC is one with a viscosity in 2 wt% aqueous solution of 1000 to 4000 mPa.s. Viscosity measurements are done using a
 5 Brookfield viscometer, Spindle #3, @30 rpm. Lower viscosity materials are measured using Spindle #2, @60 rpm.

HPC is an ether of cellulose in which some of the hydroxyl groups in the repeating glucose units have been hydroxy-propylated forming $-OCH_2CH(OH)CH_3$ groups using
 10 propylene oxide. The average number of substituted hydroxyl groups per glucose unit is referred to as the degree of substitution (DS). Complete substitution would provide a DS of 3. However, as the hydroxy-propyl group itself contains a hydroxyl group, this can also be etherified during preparation of HPC. When this occurs, the number of moles of hydroxy-propyl groups per glucose ring, moles of substitution (MS), can be higher than 3.

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The majority (typically around 75% for a DS of 3) of the mass of HPC is found in the substituent groups rather than the backbone.

20 Also, nonionic polysaccharides selected from the group consisting of: hydroxy-propyl methyl cellulose, hydroxy-ethyl methyl cellulose, hydroxy-propyl guar, hydroxy-ethyl ethyl cellulose and methyl cellulose may be used.

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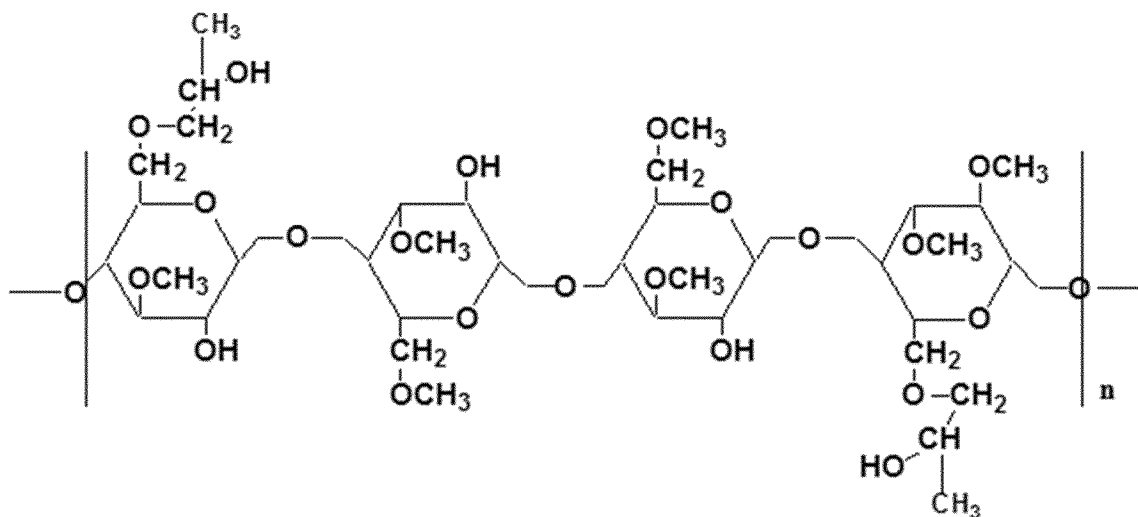
The ring spacing of these β -1,4-linked polymers is such that each alternate ring of the polymer is well placed to allow a pseudo hydrogen-bond interaction with the pi-electron clouds of the phthalate rings in polyester. Moreover, these polymers have a balance of hydrophobicity and hydrophilicity which means that they are able to interact with a fabric without being so hydrophobic as to be insoluble. Other nonionic, modified polysaccharides, for example hydroxyl-ethyl cellulose, do not have the correct properties and show poor performance as deposition polymers, especially on polyester.

In those ethers of cellulose in which some of the hydroxyl groups in the repeating glucose units have been hydroxy-alkylated the average number of substituted hydroxyl groups per glucose unit is referred to as the degree of substitution (DS). Complete substitution would provide a DS of 3. However, if the substituent group itself contains a hydroxyl group, this can also be etherified. When this occurs, the number of moles of substituent groups per glucose ring, moles of substitution (MS), can be higher than 3.

Some of the -OH groups (where present) in the hydroxyl-alkyl pendant group may be replaced with alkyl ethers. Typically these are C₁-C₂₀ alkyl ethers, and may, in specific cases be C₁₆-C₂₂ ethers. The most preferred alkyl chain is stearyl.

Hydroxy-propyl methyl cellulose (HPMC), has the repeat structure shown in generalised terms below:

- 9 -



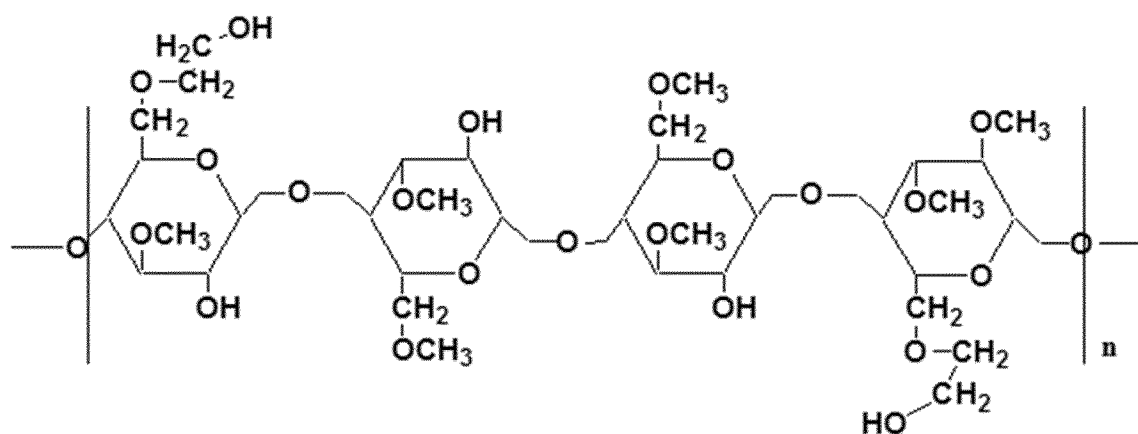
Since the hydroxypropoxy substituents can be attached to each other on side chains, the degree of substitution for HPMC can be higher than 3.

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In useful derivatives of HPMC "Sangelose" some of the -OH groups in the hydroxyl-propyl pendant group are replaced with alkyl ethers. Typically these are C₁-C₂₀ alkyl ethers, and may, in specific cases be C₁₆-C₂₂ ethers. The most preferred alkyl chain is stearyl.

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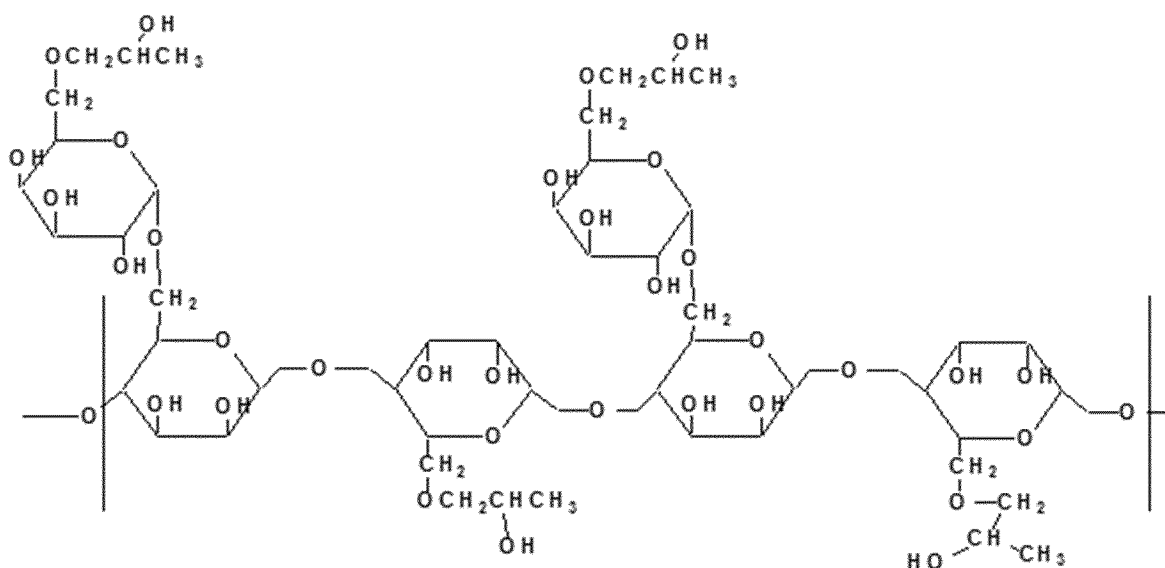
Hydroxy-ethyl methyl cellulose (HEMC), has the repeat structure shown in generalised terms below:



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Since the ethoxy substituents can be attached to each other on side chains, the degree of
 5 substitution can be higher than 3.

Hydroxy-propyl guar (HPG), has the repeat structure shown in generalised terms below:

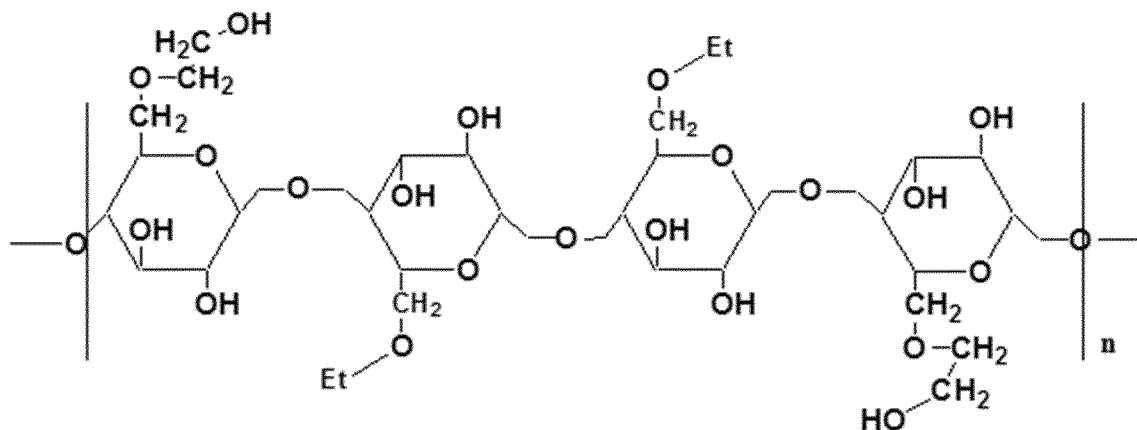


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Since the hydroxypropoxy substituents can be attached to each other on side chains, the
 15 degree of substitution in HPG can be higher than 3.

Hydroxy-ethyl ethyl cellulose (HEEC), has the repeat structure shown in generalised
 terms below:

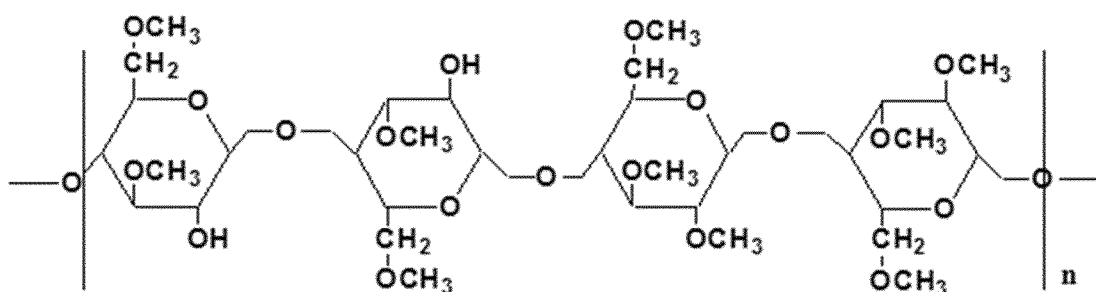
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HEEC is less preferred than other nonionic polysaccharide delivery aids disclosed herein.

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Methyl cellulose (ME), has the repeat structure shown in generalised terms below:



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The theoretical maximum degree of substitution (DS) is 3.0. However, more typical values are 1.3 to 2.6.

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Especially good results may be obtained when the deposition polymer is one which has a viscosity in 2 wt% aqueous solution of over 1000 mPa.s. Viscosity measurements are made using a Brookfield viscometer, Spindle #3, @30 rpm. Lower viscosity materials are measured using Spindle #2, @60 rpm.

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Preferably the nonionic polysaccharide deposition polymer has a molecular weight above 50 kDa and more preferably above 140 kDa, most preferably above 500 kDa. As the molecular weight is increased the performance of the deposition polymer generally
5 increases.

DS is typically in the range from 1.0 to 3, more preferably above 1.5 to 3, most preferably, where possible from 2.0 to 3.0.

10 A typical MS for the deposition polymer is 1.5 to 6.5. Preferably the MS is in the range from 2.8 to 4.0, more preferably above 3.0, most preferably from 3.2 to 3.8.

Preferably, the deposition-aid polymer is present at levels such that the ratio, polymer : particle solids, is in the range 1:500 to 3:1, more preferably 1:500 to 1:2 and most,
15 preferably 1:200 to 1:2.

The Polyurea

20 Polyureas are formed from diisocyanates or polyisocyanates with diamines or polyamines. Normally to make a microcapsule the cyanate part is present in a dispersed (oily) phase and the amine part is present in the continuous (aqueous) phase. The shell forms via interfacial polymerisation at the phase interface. This reaction and the manufacture of polyurea shell microcapsules is widely known and understood to the
25 skilled person and the invention can be applied to any type of polyurea microcapsule.

When a diisocyanate is used it may be linear aliphatic, cycloaliphatic or aromatic.

Suitable, aromatic polyisocyanates comprise, but are not limited to, 2,4-and 2,6-toluene
30 diisocyanate, naphthalene diisocyanate, diphenyl methane diisocyanate and triphenyl methane-p,p'p"- trityl triisocyanate, polymethylene polyphenylene isocyanate, 2,4,4'-diphenylether triisocyanate, 3,3'-dimethyl-4,4'- diphenyl diisocyanate, 3,3'-dimethoxy-4,4'diphenyl diisocyanate, and 4,4'4"-triphenylmethane triisocyanate.

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Suitable aliphatic polyisocyanates comprise, but are not limited to dicyclohexylmethane 4,4'-diisocyanate, hexamethylene-1,6-diisocyanate, isophorone diisocyanate, trimethyl-hexamethylene diisocyanate, trimer of hexamethylenel,6-diisocyanate, trimer of
 5 isophorone diisocyanate, 1,4-cyclohexane diisocyanate, urea of hexamethylene diisocyanate, trimethylene diisocyanate, propylene-1,2-diisocyanate and butylenes-1,2-diisocyanate and mixtures thereof.

Suitable diamines can comprise amines such as ethylene diamine (EDA), phenylene
 10 diamine, toluene diamine, hexamethylene diamine, diethylenetriamine, tetraethylene pentaamine, pentamethylene hexamine, 1,6-hexane diamine, Methylene tetramine, 2,4-diamino-6-methyl- 1,3,5 triazine 1,2-diaminocyclohexane, 4,4'-diamino-diphenylmethane, 1,5-diaminonaphthalene, 2,4,4'- triaminodiphenylether, bis(hexa-methylenetriamine), 1,4,5,8-tetraaminoanthraquinone, isophorone diamine, diamino propane and
 15 diaminobutane, and mixtures thereof. Polymeric amines may also be used, for example Jeffamines (polyether amine) and poly(ethyleneimine).

Water soluble diamine or amine salt or polyamines or polyamines salts are preferred as the amine is usually present in the aqueous phase. Combinations of Polyisocyanates
 20 and diamines are preferred because the plural functionality enables networked structures and having the plural functional material in the disperse phase reduces the chance of bonds forming between adjacent particles and clumping resulting

Other suitable materials are disclosed, for example, in US2014/0017287. Isocyanate-
 25 based capsule wall technologies are also disclosed in WO 2004/054362; EP 0 148149; EP 0 017 409; U.S. 4,417,916, U.S. 4,124,526, US 6,566,306, US 6,730,635, WO 90/08468, WO 92/13450, US 4,681, 806, US 4,285,720, US 6,340,653 and EP 2673078.

The benefit agent

30 A benefit agent is a material that when deposited onto a substrate imparts some desirable effect to that substrate. As such it comprises a wide selection of materials. Because polyurea capsules are made by interfacial polymerisation from an oil in water

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emulsion the benefit agent is generally a hydrophobic material that is miscible with an oil phase or forms the oil phase.

Suitable benefit agents include perfume raw materials (also referred to herein as
5 fragrance), silicone oils, waxes, hydrocarbons, higher fatty acids, essential oils, lipids, skin coolants, vitamins, sunscreens, antioxidants, malodour reducing agents, odour controlling materials, skin softening agents, insect and moth repelling agents, colorants, chelants, sanitization agents, germ control agents, skin care agents, natural actives, antibacterial actives, preservatives, chemosensates, (for example menthol), sunless-
10 tanning agents (for example dihydroxyacetone), emollients (for example sunflower oil and petrolatum), antiaging agents, anti-inflammatory agents, skin conditioning agents, skin lightening agents and mixtures thereof.

Preferred benefit agents are fragrance, anti-aging agents, antimicrobial agents, anti-
15 bacterial agents, anti-fungal agents, lubricants and shading dyes. Other possible benefit agents include: anti-oxidants, vitamins, anti-inflammatory actives, skin lightening agents, skin conditioning agents, for example 12-hydroxy stearic acid, oils, insect repellents and sunscreens. These are described in detail in the literature. For example: WO13/026657 and WO12/022736.

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Optional materials in the microcapsule (including wall)

Isocyanate must be soluble in whatever will form the microcapsule core so additional material may be needed if the benefit agent does not dissolve the isocyanate.

5

The microcapsule may therefore optionally comprise a carrier oil (also referred to herein as a diluent). It will be clear to a skilled person which oils are suitable for use with a certain benefit composition. The carrier oils are hydrophobic materials that are miscible in the benefit agent materials used in the present invention. Suitable oils are those having reasonable affinity for the benefit agent. Suitable materials include, but are not limited to triglyceride oil, mono and diglycerides, mineral oil, silicone oil, diethyl phthalate, polyalpha olefins, castor oil and isopropyl myristate. Preferably, the oil is a triglyceride oil, most preferably a capric/caprylic triglyceride oil.

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Many emulsifying agents are known for use in emulsion polymerisation. Suitable emulsifying agents for use in the polymerisation process may comprise, but are not limited to, nonionic surfactants such as polyvinylpyrrolidone (PVP), polyethylene glycol sorbitan monolaurate (Tween 20), polyethylene glycol sorbitan monopalmitate (Tween 40), polyethylene glycol sorbitan monooleate (Tween 80), polyvinyl alcohol (PVA), and poly(ethoxy)nonyl phenol, ethylene maleic anhydride (EMA) copolymer, Easy-Sperse™ (from ISP Technologies Inc.), ionic surfactants such as partially neutralized salts of polyacrylic acids such as sodium or potassium polyacrylate or sodium or potassium polymethacrylate. Brij™-35, Hypermer™ A 60, or sodium lignosulphate, and mixtures thereof.

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Emulsifiers may also include, but are not limited to, acrylic acid-alkyl acrylate copolymer, poly(acrylic acid), polyoxyalkylene sorbitan fatty esters, polyalkylene co-carboxy anhydrides, polyalkylene co-maleic anhydrides, poly(methyl vinyl ether-co-maleic anhydride), poly(propylene-co-maleic anhydride), poly(butadiene co-maleic anhydride), and poly(vinyl acetate-co-maleic anhydride), polyvinyl alcohols, polyalkylene glycols, polyoxyalkylene glycols, and mixtures thereof.

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Preferred emulsifying agents are fatty alcohol ethoxylates (particularly of the Brij™ class), salts of ether sulphates (including SLES), alkyl and alkaryl sulphonates and sulphates (including LAS and SDS) and cationic quaternary salts (including CTAC and CTAB).

5 Typically a co-surfactant will be present in the dispersed phase and in the resulting particle. Suitable co-surfactants for use in the present invention include hexadecane, cetyl alcohol, lauroyl peroxide, n-dodecyl mercaptan, dodecyl methacrylate, stearyl methacrylate, polystyrene, polydecene, mineral oils, isopropyl myristate, C₁₂-C₁₅ alkyl benzoate and polymethyl methacrylate.

10

The preferred cosurfactants comprise hexadecane, polydecene and isopropyl myristate.

As a wt% of oil phase as a total, the co-surfactant is typically 0 to 20 wt%, preferably 1 to 15 wt%, more preferably 2 to 12.5 wt%.

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In the prior art it has been suggested that pure polyurea shell walls are not useful due to their inherent leakiness. Inclusion of materials such as Carboxymethyl cellulose into the wall is taught as are more complex shell walls made of mixtures of polyurea and other polymers. In the present invention it is advantageous for the capsule wall to be at least 95% and preferably substantially 100% polyurea. Capsule leakiness can be adjusted by wall thickness and choice of the amine(s) and isocyanate(s). For some applications, e.g. laundry, it is desirable that some benefit agent leaks from the capsule before it ruptures. When the benefit agent is a perfume this can increase freshness perception when the washing is still wet.

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Size of microcapsule

Generally, the microcapsules will have an average diameter of from about 0.001 to about 1,000 microns, preferably from about 1 to about 500 microns, more preferably from about 5 to about 100 microns, and even more preferably from about 10 to about 50 microns. These dimensions can play an important role in the ability to control the application of the microcapsule composition in the practice of the present invention. The broadest range of

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microcapsule size under any conditions would be about 0.001 to about 1,000 microns and a more easily sprayed size limit would be between about 10 and about 50 microns.

5 It is desirable for a suspension of microcapsules to contain a dispersant also in order to prevent microbial contamination it is desirable that the microcapsule composition contains a preservative. The preservative may be contained in the core material and/or in the aqueous carrier.

Uses of the microcapsules and suitable compositions

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The compositions for use in the invention may contain one or more other ingredients in addition to the polyurea microcapsules with nonionic polysaccharide deposition polymer. They may contain other types of microcapsules or similar microcapsules with a different benefit agent inside.

15

In addition to any fragrance formulation that may be contained within the microcapsules, a composition comprising microcapsules of the present invention may also contain free perfume.

20 Formulated compositions comprising the particles of the invention may contain a surface-active compound (surfactant) which may be chosen from soap and non-soap anionic, cationic, nonionic, amphoteric and zwitterionic surface active compounds and mixtures thereof. Many suitable surface 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. The preferred surface-active compounds that can be
25 used are soaps and synthetic non soap anionic, and nonionic compounds.

Depending on the end use of the composition comprising the microcapsules other materials commonly found in such compositions may be used as usual. The one main exception is that free cellulase is preferably absent from the composition unless it is
30 somehow deactivated. Mannanase is also desirably avoided.

Such ingredients include preservatives (e.g. bactericides), pH buffering agents, perfume carriers, anti-redeposition agents, soil-release agents, polyelectrolytes, anti-shrinking

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agents, anti-wrinkle agents, anti-oxidants, sunscreens, anti-corrosion agents, drape imparting agents, anti-static agents, pearlisers and/or opacifiers, natural oils/extracts, processing aids, e.g. electrolytes, hygiene agents, e.g. anti-bacterials and antifungals, thickeners, skin benefit agents, colorants, whiteners, optical brighteners, soil suspending agents, deterative enzymes, compatible bleaching agents (particularly peroxide compounds and active chlorine releasing compounds), gel-control agents, freeze-thaw stabilisers, bactericides, preservatives (for example 1,2-benzisothiazolin-3-one), hydrotropes, perfumes and mixtures thereof.

- 10 The compositions for use in the invention may also contain pH modifiers such as hydrochloric acid or lactic acid.

The end-product compositions of the invention may be in any suitable physical form e.g. a solid such as a solid bar, a paste; or a liquid or gel, preferably, an aqueous-based liquid.

- 15 Laundry detergents, skin cleansing compositions and hair conditioners are preferred compositions for use with the microcapsules.

- 20 The microcapsules are typically included in compositions at levels of from 0.01% to 10%, preferably from 0.5% to 7%, most preferably from 0.5% to 5% by weight of the total composition.

- 25 The invention will now be further described with reference to the following non-limiting examples.

EXAMPLES**Example 1 – Synthesis of Polyurea Microcapsule with Xyloglucan Added at Various Addition Times**

5 A number of polyurea microcapsules were synthesised, whereby the xyloglucan deposition polymer was added over various addition times, once the encapsulating process had begun. The materials used are given in Table 1 and composition details are given in Table 2.

Table 1

Material	Supplier	% Active
Benzyl Acetate	Aldrich	>99%
Hostasol Yellow 3G	Clariant	100%
Poly(methylene(polyphenyl)isocyanate)	Polysciences	100% Active (30% Isocyanate)
LAS (Linear Alkyl Benzene Sulphonate, Sodium Salt)	Petrelabs	90%
Hexamethylene Diamine	Aldrich	98%
Xyloglucan	DSP Gokyo Food and Chem. Co.	100%

10 Table 2

Particle Solids (%) =	15
% BA (on solids) =	89.6
% Hostasol (on oil phase)=	0.02
% PMPHI (on solids) =	7.2
%HMDA (on solids) =	3.2
Total Wt (g) =	200
%XG (on solids) =	2.0

- 20 -

The microcapsules were made using the following synthesis:

- 1) 0.0054 g of Hostasol yellow 3G and 2.2 g of poly(methylene(polyphenyl)isocyanate) were dissolved in 26.9 g of benzyl acetate (oil phase).
- 2) 0.77 g of LAS (linear alkyl benzene sulfonate) was dissolved in 100 ml of deionised water by stirring for 30 minutes (aqueous phase).
- 3) A 1 wt% xyloglucan (XG) solution was prepared separately by homogenising (8,000 rpm) 5 g XG in 495 g of boiled distilled water for 5 minutes and allowing to cool before use.
- 4) The oil and aqueous phases were mixed and emulsified using a homogeniser (5,000 rpm) for 2 minutes (care was taken to avoid excessive foaming).
- 5) This mixture was constantly stirred using an overhead stirrer (200 rpm).
- 6) The water for solids adjustment was added (64.2 g for XG free sample and 4.2 g for all XG containing samples).
- 7) Then 0.96 g hexamethylene diamine dissolved in 5 g of deionised water was added dropwise.
- 8) Numerous samples were prepared, one where no XG solution was added (control) and the others whereby 60 g of the 1wt% XG solution was added after 7, 15, 30, 45 or 60 minutes.
- 9) Polyurea curing was allowed to proceed at room temperature for at least 3 hours.

Example 2 – Deposition Assessment via Fluorescence Depletion

1) Preparation of Wash Liquor Stock Solutions

A concentrated wash liquor stock solution (10X) was prepared using the materials in Table 3.

Table 3

Component	Active (%)	Amount (g)
LAS (Linear Alkyl Benzene Sulphonate, Sodium Salt)	90.0%	5.5
Neodol 25-7	100.0%	5.0
Na ₂ CO ₃	100.0%	7.55
NaHCO ₃	100.0%	2.42
Deionised water	N/A	979.5

2) Preparation of the wash liquor:

The wash liquor stock (10 ml) and deionised water (90 ml) were added to a 125 ml plastic bottle. This gave 100 ml of wash liquor buffered to pH 10.5 and containing 1 g/L surfactant (50:50 LAS:Neodol 25-7).

3) Simulated Wash:

0.005 g (50 ppm on wash liquor) of microcapsule particles were added to the plastic bottle containing wash liquor and agitated slightly to ensure mixing. (Washes were done in duplicate for each sample and results averaged). A 5 ml aliquot was taken from each and the fluorescence (excitation = 450 nm, emission = 515, slit width = 15) measured in a 1 cm cuvette using a fluorimeter (Perkin Elmer LS50). This fluorescence value represents 100% particles in the wash solution prior to the simulated wash process.

A section of unfluoresced cotton measuring 20 cm by 20 cm was placed into each plastic bottle containing the wash liquor and microcapsules and the bottle sealed.

The bottles were agitated at 40 °C and 150 rpm using a water shaker bath (Haake SWB25) for 45 minutes to simulate the main wash.

The cloths were then removed and wrung by hand and a 5 ml aliquot of the remaining wash liquor was taken and the fluorescence measured (as before). From interpolation of a concentration versus fluorescence calibration curve, the concentration of the microcapsules remaining in the liquor after the wash could be determined and hence the percentage deposited (wash deposition) on cloth determined by difference.

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The plastic bottles were then thoroughly rinsed and the 'wrung' cloths returned to the bottles and 100 ml of de-ionised water was added and the bottles sealed. The bottles were then agitated (150 rpm) on the water shaker bath for 10 minutes at ambient temperature (~20°C) to simulate a rinse procedure. The clothes were then removed and wrung by hand. A 5 ml aliquot of the rinse solution was taken and the fluorescence determined as before. Again, interpolation of the calibration plot allowed the microcapsule concentration removed from the cloth during the rinse to be determined and, by subtraction from the level deposited after the main wash, the overall percentage deposition was determined.

- 10 The percentage depositions (after main wash and rinse) for the samples prepared in Example 1) are shown in Table 4.

Table 4

Polyurea - XG Addition Time	Main Wash		After Rinse	
	Depo (%)	SD	Depo (%)	SD
Control (No XG)	58.4	5.0	44.5	5.6
After 7 mins	69.9	5.3	46.4	13.2
After 15 mins	83.1	3.0	72.6	0.1
After 30 mins	79.9	1.9	69.5	3.1
After 45 mins	86.3	4.4	73.3	1.2
After 60 mins	85.3	1.1	69.0	2.8

The results show that deposition is enhanced by the attachment of xyloglucan and that for maximum deposition, the xyloglucan should not be added until 15 minutes into the reaction. After this time, addition up to one hour is possible without detriment to deposition performance.

Example 3 – Synthesis of Comparative Melamine Formaldehyde Microcapsule

- 25 A comparative example prepared at equivalent composition levels and a xyloglucan addition time point of 15 minutes into microcapsule formation was prepared, with the

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difference that melamine formaldehyde was used as shell material (rather than polyurea) and the reaction was carried out at 75°C for 3 hours. The composition details are given in Table 5 and the materials used in Table 6.

Table 5

Particle Solids (%)	15.0
Benzyl Acetate (% on solids)	89.6
Hostasol (% on oil phase)	0.02
Melamine Formaldehyde (% on solids)	10.4
Xyloglucan (% on solids)	2.0
Total Weight (g)	200

5 Table 6

Material	Supplier	% Active
Melamine	Aldrich	100%
Formaldehyde Solution (Formalin)	Aldrich	37.0%
Benzyl Acetate	Aldrich	>99%
Sodium Chloride	Aldrich	>99%
Xyloglucan	DSP Gokyo Food and Chem. Co.	100%
Formic Acid	Aldrich	>96%
Sodium Carbonate	Aldrich	>99%

Synthesis:

Melamine Formaldehyde Pre-Polymer Synthesis

- 1) To a 250 ml reaction flask was added 19.5 g formalin (37 wt% aqueous formaldehyde) and 44 g water.
- 2) The pH of the solution was adjusted to 8.9 using 5 wt% sodium carbonate aqueous solution.
- 3) 10 g melamine and 0.6 g sodium chloride were added and the mixture stirred at 200 rpm using an overhead stirrer.

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4) The mixture was heated to 62 °C and stirring continued until the mixture became clear (typically 1 hour). This solution contains 23.2 wt% trimethylol melamine and is hereinafter referred to as pre-polymer (1).

5 Xyloglucan Grafted Melamine Formaldehyde Microcapsule Synthesis

A number of xyloglucan grafted microcapsules were prepared containing 2, 1 or 0.5% xyloglucan (on particle weight). The weights used are given Table 7.

Table 7

Material:	2% XG	1% XG	0.5% XG
Pre-Polymer (1)	13.4	13.4	13.4
Benzyl Acetate	26.9	26.9	26.9
Hostasol Yellow 3G	0.0054	0.0054	0.0054
Water	99.7	129.7	144.7
1% Xyloglucan Solution	60.0	30.0	15.0

10

The xyloglucan solution was prepared by dissolving 2 g of xyloglucan in 198 g of boiled water, using a homogeniser at 8,000 rpm for 5 minutes and allowing to cool prior to using.

- 1) The water was added to a 250 ml reaction flask and heated to 75°C.
- 15 2) The pre-polymer (1) was then added, and the pH was adjusted to 4.1 using 10 wt% formic acid.
- 3) After approximately 1 minute the solution became turbid.
- 4) A homogeniser (at 8,000 rpm) was then used to agitate the mixture while slowly adding the benzyl acetate over ~30seconds.
- 20 5) The mixture was agitated at this shear regime for a further 2 minutes.
- 6) The reaction vessel was then sealed and heated with overhead stirring (300 rpm) at 75°C.
- 7) The xyloglucan solution was added after 15 minutes.
- 8) The reaction was allowed to continue for a total of 3 hours.
- 25 9) The mixture was cooled and adjusted to pH 7 using 5 wt% sodium carbonate

- 25 -

The final dispersions were 15% particle solids, consisting of approximately 10% MF shell and 90% Benzyl Acetate, with 2 to 0.5% XG (on particle solids) attached.

Example 4 – Comparison of Particle Size of Xyloglucan Grafted Polyurea and Melamine Formaldehyde Microcapsules

- 5 The particle size for both the polyurea (PU) and melamine formaldehyde (MF) synthesized microcapsules was measured (using a Malvern Mastersizer 2000). The results are given in Table 8.

Table 8

	Particle Size	d(0.5) microns
XG Level (%)	PU	MF
2	15.6	139.1
1	14.9	20.7
0.5	14.9	17.3

- 10 The PU synthesis route generates smaller particles and allows the incorporation of higher XG levels without inducing aggregation and increasing particle size.

Example 5 – Comparison of Laundry Liquid Stability of Xyloglucan Grafted Polyurea and Melamine Formaldehyde Microcapsules

- 15 The stability of the PU and MF microcapsules as used in Example 4 were compared within an unstructured laundry liquid detergent with composition in Table 9 (1 wt% of microcapsules added).

Table 9

Component	% w/w
Monopropylene Glycol	11
Glycerol	5
Monoethanolamine	7
Triethanolamine	2.5
Citric Acid	3.9
Neodol 25-7	4.6
LAS Acid	8.8
Prifac 5908	3
Dequest 2010	1.5
SLES 3EO	6.8
EPEI (Sokalan HP 20)	3
Acusol OP301	0.1
Sodium Sulphite	0.25
Water	to 100%

- Attachment of a nonionic polysaccharide to a microcapsule might be expected to slightly stabilize a dispersion of the particles. Surprisingly the same deposition polymer when added to polyurea microcapsules gave a visibly much more stable suspension of the particles after 3 days, whereas the corresponding melamine formaldehyde capsules with the same level of the same deposition polymer attached visibly settled out of the detergent liquid much more over the same time period.

Example 6 – Synthesis of Full Perfume Polyurea Microcapsule with Grafted Hydroxypropyl Cellulose

- 10 This example details the production of hydroxypropyl cellulose (HPC) grafted polyurea encapsulates containing a model perfume (rather than benzyl acetate only) and low levels of hydroxypropyl cellulose (0.3% on encapsulate weight). The materials used are similar to those in Example 1, with the exceptions that AKK perfume replaces benzyl acetate, 5% polyvinyl alcohol aqueous solution replaces 0.5% LAS solution and 1% hydroxypropyl

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cellulose aqueous solution replaces 1% XG solution. New material details are given in Table 1 and composition details are given in Table 2.

Table 10

Material	Supplier	% Active
AKK Perfume	Aldrich (for ingredients) – See Table 11 for composition	100%
Polyvinyl Alcohol (Mowiol 18-88)	Aldrich	100%
Hydroxypropyl Cellulose (MW = 370K)	Aldrich	100%

5 Table 11 (AKK Perfume Composition)

Wt%	Ingredient	CAS
6.66	Manzanate	39255-32-8
6.66	Aldehyde C8	124-13-0
6.66	Tetra hydro linalol	78-69-3
6.66	Benzyl acetate	140-11-4
6.66	Linalyl acetate	115-95-7
11.7	OTBCA	88-41-5
1.66	Damascone, delta	57378-68-4
6.66	Aldehyde c12	112-54-9
6.66	Verdyl acetate	5413-60-5
6.66	Ionone beta	14901-07-6
6.66	Bangalol	28219-61-6
6.66	Iso E super (OTNE)	54464-57-2
6.66	Hexyl cinnamic aldehyde	101-86-0
6.66	Cyclopentadecanolide	106-02-5
6.66	Phenyl ethyl 2-phenylacetate	102-20-5

The weights and procedure were identical to that given in Example 1. The HPC solution was added 15 minutes after the reaction started.

The final dispersion was 10% particle solids, consisting of approximately 10% PU shell and 90% AKK Perfume, with 0.3% HPC (on particle solids) attached.

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Example 7 – Synthesis of Comparative Full Perfume Melamine Formaldehyde Encapsulate with Grafted Hydroxypropyl Cellulose

A comparative example prepared at equivalent composition levels and an HPC addition time point of 15 minutes into microcapsule formation was prepared. This comparative example utilises MF shell rather than polyurea. The materials used were similar to those detailed in Example 3, with the exceptions that AKK perfume replaces benzyl acetate and 1% hydroxypropyl cellulose aqueous solution replaces 1% XG solution. New material details are given in Tables 10 and 11.

The weights and procedure were identical to that detailed in Example 3.

- 10 The final dispersion was 10% particle solids, consisting of approximately 10% MF shell and 90% AKK Perfume, with 0.3% HPC (on particle solids) attached.

Example 8 – Comparison of Laundry Liquid Stability of HPC Grafted Polyurea and Melamine Formaldehyde Microcapsules

- 15 The stability of the PU and MF microcapsules as described in Examples 6 and 7 were compared within an unstructured laundry liquid detergent. The inclusion levels and procedure were identical to that detailed in Example 5.

A clear difference in stability was observed after three days:

The MF encapsulate had completely phase separated and creamed to the top of the solution, whereas with the polyurea variant the stability is maintained.

20

Examples 9 to 15: Compositions

These examples show the use of the PU microcapsules in typical laundry, hair and skin body wash compositions. The materials used are given in Table 12.

25

Table 12

Component	Specification
LAS	Linear Alkyl Benzene Sulphonic Acid Marlon AS3, ex. Huls
Na-PAS	Primary Alkyl Benzene Sulphonic Acid, neutralises with NaOH
Dobanol 25-7	C12-15 Ethoxylated Alcohol, 7EO, ex Shell
Zeolite	Wassalith P, ex Degussa
STPP	Sodium Tri Polyphosphate, Thermphos NW, ex Hoechst
Dequest 2066	Metal Chelating Agent, ex. Monsanto
Lipolase	Type 100L, ex. Novo
Savinase 16L	Protease, ex Novo
Sokalan CP5	Acrylic/Maleic Builder Polymer, ex BASF
Deflocculating Polymer	Polymer A-11 disclosed in EP-A-346 995
SCMC	Sodium Carboxymethyl Cellulose
Texapon N 701	Sodium Laureth Sulphate, ex Cognis
Aculyn 28 Polymer (20%)	Carbomer, ex Rohm and Haas
Tegobetaine CK	Cocoamidopropyl Betaine, ex Goldschmidt
BF Jaguar C14	Guar Hydroxypropyltrimonium Chloride, ex Aqualon
DC 1788	Dimethiconol (and) TEA-Dodecylbenzenesulfonate, ex Dow Corning
Euperlan KE 4515	Glycol Distearate and Sodium Laureth Sulphate , Cocamidopropyl Betaine, ex Cognis
BTAC	Genamin BTLF, Behentrimonium Chloride, ex Aako
Cetearyl Alcohol	Lanette S3, ex. BASF
DC5 7134	Silicone Emulsion, ex Dow Corning
Carbopol Aqua SF-1	Acrylate Copolymer, Lubrizol
SLES 1EO	Sodium Lauryl Ether Sulphate (1EO), ex. BASF
Cocamide MEA	Cocamide monoethanolamine, ex Stepan
Versene XL100	Ethylenediaminetetraacetic Acid Tetrasodium Salt, ex Dow Chemical
PPG-9	Polypropylene Glycol, MW = 425g, Dow Chemical
Laundry Minors	Anti-redeposition polymers, transition-metal scavengers, bleach stabilisers, fluorescers, antifoam, dye transfer inhibition polymers, enzymes, perfume

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Example 9 – Spray-Dried Powder

Table 13 gives the composition of a spray dried laundry detergent powder containing PU microcapsules from Example 1.

5

Table 13

Component	% w/w
PU Microcapsules (from Example 1)	1.0
Na PAS	11.5
Dobanol 25-7	6.3
Soap	2.0
Zeolite	24.1
SCMC	0.6
Na Citrate	10.6
Na Carbonate	23.0
Sodium Polyacrylate (MW 1,300,000)	0.7
Dequest 2066	0.4
Sokalan CP5	0.9
Savinase 16L	0.7
Lipolase	0.1
Perfume	0.4
Water/salts	Up to 100%

Example 10 – Laundry Detergent Granulate Prepared by Non-Spray Drying Method

10

Table 14 gives a granular laundry detergent composition containing the PU microcapsules of Example 1, as can be manufactured by a non-tower route.

15

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Table 14

Component	% w/w
PU Microcapsules (from Example 1)	1.0
Na PAS	13.5
Dobanol 25-7	2.5
STPP	45.3
Na Carbonate	4.0
Polyacrylamide (MW 5,500,000)	2.8
Na Silicate	10.1
Perfume	1.0
Minors	1.5
Water	Up to 100%

5 **Example 11 – Isotropic Laundry Liquid**

Table 15 gives an isotropic laundry liquid composition incorporating the PU microcapsules of Example 1.

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Table 15

Component	% w/w
PU Microcapsules (from Example 1)	1.0
Na Citrate	10.7
Propylene Glycol	7.5
Ethylene Glycol	4.5
Borax	3
Savinase 16L	0.3
Lipolase	0.1
Dextran (MW 800,000)	1.0
Monoethanolamine	0.5
Cocofatty Acid	1.7
NaOH (50%)	2.2
LAS	10.3
Dobanol 25-7	6.3
LES	7.6
Perfume	1.0
Minors (adjust pH to 7 with NaOH)	1.3
Water	Up to 100%

5

Example 12 – Structured Laundry Liquid

Table 16 gives a structured liquid laundry detergent composition incorporating the PU microcapsules of Example 1.

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Table 16

Component	% w/w
PU Microcapsules (from Example 1)	1.0
LAS	16.5
Dobanol 25-7	9.0
Oleic Acid (Priolene 6907)	4.5
Zeolite	15.0
KOH (neutralising acids to pH 7)	8.5
Citric Acid	8.2
Deflocculating Polymer	1.0
Protease	0.38
Lipolase	0.2
Imacol C (ex Clariant)	2.0
Perfume	1.0
Minors	0.4
Water	Up to 100%

Example 13 – Hair Shampoo

5

Table 17 gives a hair shampoo composition incorporating the PU microcapsules of Example 1.

- 34 -

Table 17

Composition	% w/w
PU Microcapsules (from Example 1)	1.0
Texapon N701	12.8
Aculyn 28 Polymer (20%)	1.0
Tegobetaine CK	1.6
BF Jaguar C14	0.15
DC 1788	3.0
Emperlan KE 4515	2.5
Propylene Glycol	0.25
Sodium Hydroxide	0.2
Perfume	2.0
Water	Up to 100%

Example 14 – Hair Conditioner

5

Table 16 gives a hair conditioner composition incorporating the PU microcapsules of Example 1.

Table 16

10

Composition	% w/w
PU Microcapsules (from Example 1)	1.0
BTAC	2.9
Cetearyl Alcohol	4.0
DC5 7134	2.5
Perfume	1.0
EDTA	0.1
Potassium Chloride	0.1
Water	Up to 100%

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Example 15 – Skin Body Wash

Table 17 gives a skin body wash composition incorporating the PU microcapsules of Example 1.

5

Table 17

Composition	% w/w
PU Microcapsules (from Example 1)	1.0
Carbopol Aqua SF-1	1.2
SLES 1EO	11.0
Cocamide MEA	1.0
EDTA	0.05
PPG-9	0.1
NaCl (25% solution)	1.0
Perfume	1.0
NaOH (50% solution)	0.01
Water	Up to 100%

Examples 9 to 15 may alternatively be formulated using the HPC grafted microcapsule from Example 6.

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Claims

1. A microcapsule containing a benefit agent inside a polyurea shell characterised in that the polyurea has a nonionic polysaccharide deposition polymer covalently bonded to it.
5
2. A microcapsule according to claim 1 in which the deposition polymer is a nonionic polysaccharide selected from the group consisting of mannan, glucan, glucomannan, xyloglucan, hydroxyalkyl cellulose, dextran, galactomannan and mixtures thereof.
10
3. A microcapsule according to claim 2 in which the deposition polymer is selected from the group consisting of xyloglucan, galactomannan, dextran and hydroxypropyl cellulose.
- 15 4. A microcapsule according to claim 3 in which the deposition polymer is xyloglucan or hydroxypropyl cellulose.
5. A microcapsule according to any preceding claim in which the weight ratio of deposition polymer to polyurea shell lies in the range 1:500 to 1:2.
20
6. A microcapsule according to any preceding claim in which the nonionic polysaccharides have a molecular weight Mw in excess of 40 kDa.
7. A microcapsule according to any preceding claim comprising from 1 to 30 wt% polyurea shell.
25
8. A microcapsule according to any preceding claim in which the deposition polymer levels are from 0.1 to 10 wt%, based on microcapsule weight.
- 30 9. A microcapsule according to any preceding claim in which the polyurea is formed by the reaction of poly-isocyanate and diamine.

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10. A composition including at least 0.01 wt% of the microcapsules as claimed in any one of claims 1 to 9 and a surfactant or cationic material.

5 11. A laundry detergent composition according to claim 10 comprising at least 5 wt% anionic surfactant.

12. A skin cleansing composition or hair shampoo composition according to claim 10 comprising at least 2 wt% surfactant.

10 13. A hair conditioner composition according to claim 10 comprising at least 1 wt% cationic material.

14. A composition according to any one of claims 10 to 13 further comprising at least 0.1 wt% perfume.

15

15. A method of making the microcapsule of any one of claims 1 to 9 wherein the nonionic polysaccharide is added at least 15 minutes after commencement of curing of the polyurea.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/059321

A. CLASSIFICATION OF SUBJECT MATTER
INV. C11D17/00 C11D3/37 C11D3/22
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C11D

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

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

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2013/330292 A1 (LEI YABIN [US] ET AL) 12 December 2013 (2013-12-12) paragraph [0071]; claims 1,17,18 -----	1-15
Y	WO 2013/026657 A1 (UNILEVER PLC [GB]; UNILEVER NV [NL]; UNILEVER HINDUSTAN [IN]; CHEN HON) 28 February 2013 (2013-02-28) page 19, line 7 - line 24 -----	1-15
A	WO 2014/079745 A2 (UNILEVER PLC [GB]; UNILEVER NV [NL]; CONOPCO INC DBA UNILEVER [US]) 30 May 2014 (2014-05-30) claims 1,8 -----	1-15
A	WO 2007/062833 A1 (UNILEVER PLC [GB]; UNILEVER NV [NL]; LEVER HINDUSTAN LTD [IN]; FERGUSO) 7 June 2007 (2007-06-07) cited in the application claims 1-13 -----	1-15



Further documents are listed in the continuation of Box C.



See patent family annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2013330292 A1	12-12-2013	US 2013330292 A1	12-12-2013
		US 2016193122 A1	07-07-2016
WO 2013026657 A1	28-02-2013	AR 087664 A1	09-04-2014
		CA 2843493 A1	28-02-2013
		CL 2014000429 A1	25-07-2014
		EP 2747742 A1	02-07-2014
		ES 2569045 T3	06-05-2016
		JP 2014524499 A	22-09-2014
		US 2014206587 A1	24-07-2014
		WO 2013026657 A1	28-02-2013
WO 2014079745 A2	30-05-2014	AR 093589 A1	10-06-2015
		CN 104812447 A	29-07-2015
		EA 201590670 A1	30-10-2015
		EP 2922597 A2	30-09-2015
		JP 2016501932 A	21-01-2016
		US 2015272839 A1	01-10-2015
		WO 2014079745 A2	30-05-2014
WO 2007062833 A1	07-06-2007	AR 056827 A1	24-10-2007
		AT 540100 T	15-01-2012
		BR PI0619080 A2	20-09-2011
		CA 2630581 A1	07-06-2007
		CN 101336287 A	31-12-2008
		EP 1954796 A1	13-08-2008
		EP 2319910 A2	11-05-2011
		ES 2380376 T3	11-05-2012
		US 2009275494 A1	05-11-2009
		WO 2007062833 A1	07-06-2007
		ZA 200804678 A	27-01-2010