

PROCESS FOR PREPARING MICROCAPSULES

Technical Field

The present invention relates to a new process for the preparation of core-shell microcapsules. Microcapsules are also an object of the invention. Consumer products comprising said microcapsules, in particular perfumed consumer products or flavoured consumer products are also part of the invention.

Background of the Invention

One of the problems faced by the perfume and flavour industry lies in the relatively rapid loss of olfactive benefit provided by active compounds due to their volatility. The encapsulation of those active substances provides at the same time a protection of the ingredients there-encapsulated against “aggressions” such as oxidation or moisture and allows, on the other hand, a certain control of the kinetics of flavour or fragrance release to induce sensory effects through sequential release.

There is still a need to provide new microcapsules, while not compromising on their performance, in particular in terms of stability in a consumer product, as well as in delivering a good performance in terms of hydrophobic material delivery.

The present invention is proposing a solution to the above-mentioned problem, based on a new process for the preparation of core-shell microcapsules formed from protein/polysaccharides complexes.

Summary

It has now been found that performing microcapsules encapsulating hydrophobic material, preferably active ingredients could be obtained by interacting a polysaccharide with an oil-in water emulsion stabilized with a protein, followed by the denaturation of the protein, to form the wall of the microcapsules. The process of the invention therefore provides a solution to the above-mentioned problems as it allows preparing microcapsules with the desired stability in different applications.

In a first aspect, the present invention relates to a process for preparing a core-shell microcapsules slurry, said process comprising the steps of:

- a) dispersing an oil phase comprising a hydrophobic material, preferably a flavor or a perfume, into an aqueous phase comprising a globular protein to form an oil-in-water emulsion;
- b) adding an aqueous solution comprising a polysaccharide into the oil-in-water emulsion; and
- 5 c) applying sufficient conditions to induce the denaturation of the protein so as to form core-shell microcapsules in the form of a slurry.

In a second aspect, the invention relates to a core-shell microcapsules slurry obtainable by the process as defined above.

10 In a third aspect, the invention relates to a microcapsule slurry or microcapsule powder comprising at least one microcapsule made of:

- an oil-based core comprising a hydrophobic material, and
- at least one shell comprising a protein and a polysaccharide.

In a fourth and fifth aspects, the invention relates to perfumed consumer products and
15 flavoured edible products comprising the microcapsules defined above.

Brief Description of the Figures

Figure 1 is an optical microscope picture of a microcapsule of the invention (WPI/HMP=8 (w/w)).

20 Figure 2 is a SEM picture of a microcapsule of the invention (WPI/HMP=8 (w/w)).

Figure 3 is a SEM picture of a comparative microcapsule (Pectin added before the oil-in-water emulsion).

Figure 4 is a SEM picture of a microcapsule of the invention (WPI/HMP=8 (w/w)).

Figure 5 is a SEM picture of a microcapsule of the invention (WPI/HMP=5 (w/w)).

25 Figure 6 is a SEM picture of a microcapsule of the invention (WPI/HMP=3 (w/w)).

Figure 7 is a SEM picture of a comparative microcapsule (pectin not added during the process).

Figure 8 is a SEM picture of a microcapsule of the invention (WPI/HMP=8 (w/w)).

Figure 9 is the thermogravimetric analysis at 50°C of sample D diluted five-fold.

Figure 10 represents the limonene released from microcapsules slurries dried onto a glass slide
30 and further scratched while measuring the headspace with a photoionization detector.

Figure 11 is the thermogravimetric analysis at 50°C of sample A diluted five-fold.

Figure 12 is the thermogravimetric analysis at 50°C of samples crosslinked with polyisocyanate.

Figure 13 represents the perfume leakage of microcapsules according to the invention in a shower gel base.

Figure 14 is the thermogravimetric analysis at 50°C of samples crosslinked with polyisocyanate and glutaraldehyde.

Figure 15 is the thermogravimetric analysis at 50°C of samples crosslinked with polyisocyanate.

Figure 16 represents the perfume leakage of microcapsules of the present invention in a fabric softener.

10 **Detailed description of the invention**

Unless stated otherwise, percentages (%) are meant to designate a percentage by weight of a composition.

By “active ingredient”, it is meant a single compound or a combination of ingredients.

By “perfume or flavour oil”, it is meant a single perfuming or flavouring compound or a mixture of several perfuming or flavouring compounds.

By “consumer product” or “end-product” it is meant a manufactured product ready to be distributed, sold and used by a consumer.

For the sake of clarity, by the expression “dispersion” in the present invention it is meant a system in which particles are dispersed in a continuous phase of a different composition and it specifically includes a suspension or an emulsion.

A “core-shell microcapsule”, or the similar, in the present invention it is meant that capsules have a particle size distribution in the micron range (e.g. a mean diameter ($d(v, 0.5)$) comprised between about 1 and 3000 microns) and comprise an external solid oligomers-based shell or shell and an internal continuous oil phase enclosed by the external shell. According to the invention, the wordings “mean diameter” or “mean size” are used indifferently.

Microcapsules of the present invention have a mean size preferably greater than 10 microns, more preferably greater than 15 microns, even more preferably greater than 20 microns.

According to an embodiment, microcapsules have a mean size comprised between 10 and 500 microns, preferably between 10 and 100 microns.

According to an embodiment, microcapsules have a mean size comprised between 15 and 500 microns, preferably between 15 and 100 microns.

According to an embodiment, microcapsules have a mean size comprised between 20 and 500 microns, preferably between 20 and 100 microns.

Microcapsules according to the invention are preferably not agglomerated.

The present invention provides an advantageous alternative to known microcapsules with
5 a process involving the denaturation of a protein and therefore the formation of the microcapsules wall.

Process for preparing a core-shell microcapsule slurry

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The present invention therefore relates in a first aspect to a process for preparing a core-shell microcapsules slurry, said process comprising the steps of:

- a) dispersing an oil phase comprising a hydrophobic material, preferably a flavor or a perfume, into an aqueous phase comprising a globular protein to form an oil-in-water
15 emulsion;
- b) adding an aqueous solution comprising a polysaccharide into the oil-in-water emulsion; and
- c) applying sufficient conditions to induce the denaturation of the protein so as to form core-shell microcapsule in the form of a slurry.

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Step a) dispersing an oil phase comprising a hydrophobic material, preferably a flavor or a perfume, into an aqueous phase comprising a protein to form an oil-in-water emulsion

In step a) of the process, an oil-in-water emulsion is prepared.

The oil phase comprises a hydrophobic material. Hydrophobic material according to the
25 invention can be “inert” material like solvents or active ingredients.

According to a preferred embodiment, the hydrophobic material is a hydrophobic active ingredient and comprises preferably a perfume or flavour. Alternative hydrophobic ingredients which could benefit from being encapsulated could be used either instead of a perfume or flavour, or in combination with a perfume or flavour. Non-limiting examples of such ingredients include
30 a cosmetic, skin caring, malodour counteracting, bactericide, fungicide, pharmaceutical or agrochemical ingredient, a sanitizing agent, an insect repellent or attractant.

The nature and type of the insect control agents that can be present in the hydrophobic internal phase do not warrant a more detailed description here, which in any case would not be exhaustive, the skilled person being able to select them on the basis of its general knowledge and according to the intended use or application.

5 Examples of such insect control agents are birch, DEET (N,N-diethyl-m-toluamide), essential oil of the lemon eucalyptus (*Corymbia citriodora*) and its active compound p-menthane-3,8-diol(PMD), icaridin (hydroxyethyl isobutyl piperidine carboxylate) , Nepelactone, Citronella oil, Neem oil, Bog Myrtle (*Myrica Gale*), Dimethyl carbate, Tricyclodecenyl allyl ether, IR3535 (3-[N-Butyl-N-acetyl]-aminopropionic acid, ethyl ester, Ethylhexanediol, Dimethyl
10 phthalate, Metofluthrin, Indalone, SS220, anthranilate-based insect repellents, and mixtures thereof.

By “perfume oil” (or also “perfume”) or “flavour” what is meant here is an ingredient or composition that is a liquid at about 20°C. Said perfume or flavour oil can be a perfuming or flavouring ingredient alone or a mixture of ingredients in the form of a perfuming or flavouring
15 composition. As a “perfuming ingredient” it is meant here a compound, which is used in perfuming preparations or compositions to impart as primary purpose a hedonic effect. In other words such an ingredient, to be considered as being a perfuming one, must be recognized by a person skilled in the art as being able to at least impart or modify in a positive or pleasant way the odor of a composition, and not just as having an odor. The nature and type of the perfuming
20 ingredients present in the oil phase do not warrant a more detailed description here, which in any case would not be exhaustive, the skilled person being able to select them on the basis of its general knowledge and according to intended use or application and the desired organoleptic effect. In general terms, these perfuming ingredients belong to chemical classes as varied as alcohols, aldehydes, ketones, esters, ethers, acetates, nitriles, terpenoids, nitrogenous or
25 sulphurous heterocyclic compounds and essential oils, and said perfuming co-ingredients can be of natural or synthetic origin. Many of these co-ingredients are listed in reference texts such as the book by S. Arctander, *Perfume and Flavor Chemicals*, 1969, Montclair, New Jersey, USA, or its more recent versions, or in other works of a similar nature, as well as in the abundant patent literature in the field of perfumery. It is also understood that said ingredients may also be
30 compounds known to release in a controlled manner various types of perfuming compounds.

The perfuming ingredients may be dissolved in a solvent of current use in the perfume industry. The solvent is preferably not an alcohol. Examples of such solvents are diethyl phthalate, isopropyl myristate, Abalyn[®] (rosin resins, available from Eastman), benzyl benzoate, ethyl citrate, limonene or other terpenes, or isoparaffins. Preferably, the solvent is very hydrophobic and highly sterically hindered, like for example Abalyn[®] or benzyl benzoate. Preferably the perfume comprises less than 30% of solvent. More preferably the perfume comprises less than 20% and even more preferably less than 10% of solvent, all these percentages being defined by weight relative to the total weight of the perfume. Most preferably, the perfume is essentially free of solvent.

Preferred perfuming ingredients are those having a high steric hindrance and in particular those from one of the following groups:

- Group 1: perfuming ingredients comprising a cyclohexane, cyclohexene, cyclohexanone or cyclohexenone ring substituted with at least one linear or branched C₁ to C₄ alkyl or alkenyl substituent;
- Group 2: perfuming ingredients comprising a cyclopentane, cyclopentene, cyclopentanone or cyclopentenone ring substituted with at least one linear or branched C₄ to C₈ alkyl or alkenyl substituent;
- Group 3: perfuming ingredients comprising a phenyl ring or perfuming ingredients comprising a cyclohexane, cyclohexene, cyclohexanone or cyclohexenone ring substituted with at least one linear or branched C₅ to C₈ alkyl or alkenyl substituent or with at least one phenyl substituent and optionally one or more linear or branched C₁ to C₃ alkyl or alkenyl substituents;
- Group 4: perfuming ingredients comprising at least two fused or linked C₅ and/or C₆ rings;
- Group 5: perfuming ingredients comprising a camphor-like ring structure;
- Group 6: perfuming ingredients comprising at least one C₇ to C₂₀ ring structure;
- Group 7: perfuming ingredients having a logP value above 3.5 and comprising at least one tert-butyl or at least one trichloromethyl substituent;

Examples of ingredients from each of these groups are:

- Group 1: 2,4-dimethyl-3-cyclohexene-1-carbaldehyde (origin: Firmenich SA, Geneva, Switzerland), isocyclocitral, menthone, isomenthone, Romascone[®] (methyl 2,2-dimethyl-6-methylene-1-cyclohexanecarboxylate, origin: Firmenich SA, Geneva, Switzerland), nerone,

- terpineol, dihydroterpineol, terpenyl acetate, dihydroterpenyl acetate, dipentene, eucalyptol, hexylate, rose oxide, Perycorolle[®] ((S)-1,8-p-menthadiene-7-ol, origin: Firmenich SA, Geneva, Switzerland), 1-p-menthene-4-ol, (1RS,3RS,4SR)-3-p-mentanyl acetate, (1R,2S,4R)-4,6,6-trimethyl-bicyclo[3,1,1]heptan-2-ol, Doremox[®] (tetrahydro-4-methyl-2-phenyl-2H-pyran, origin: Firmenich SA, Geneva, Switzerland), cyclohexyl acetate, cyclanol acetate, Fructalate[®] (1,4-cyclohexane diethyldicarboxylate, origin: Firmenich SA, Geneva, Switzerland), Koumalactone[®] ((3ARS,6SR,7ASR)-perhydro-3,6-dimethyl-benzo[B]furan-2-one, origin: Firmenich SA, Geneva, Switzerland), Natactone[®] ((6R)-perhydro-3,6-dimethyl-benzo[B]furan-2-one, origin: Firmenich SA, Geneva, Switzerland), 2,4,6-trimethyl-4-phenyl-1,3-dioxane, 2,4,6-trimethyl-3-cyclohexene-1-carbaldehyde;
- 5 - Group 2: (E)-3-methyl-5-(2,2,3-trimethyl-3-cyclopenten-1-yl)-4-penten-2-ol (origin: Givaudan SA, Vernier, Switzerland), (1'R,E)-2-ethyl-4-(2',2',3'-trimethyl-3'-cyclopenten-1'-yl)-2-buten-1-ol (origin: Firmenich SA, Geneva, Switzerland), Polysantol[®] ((1'R,E)-3,3-dimethyl-5-(2',2',3'-trimethyl-3'-cyclopenten-1'-yl)-4-penten-2-ol, origin: Firmenich SA, Geneva, Switzerland), fleuramone, Hedione[®] HC (methyl-cis-3-oxo-2-pentyl-1-cyclopentane acetate, origin: Firmenich SA, Geneva, Switzerland), Veloutone[®] (2,2,5-Trimethyl-5-pentyl-1-cyclopentanone, origin: Firmenich SA, Geneva, Switzerland), Nirvanol[®] (3,3-dimethyl-5-(2,2,3-trimethyl-3-cyclopenten-1-yl)-4-penten-2-ol, origin: Firmenich SA, Geneva, Switzerland), 3-methyl-5-(2,2,3-trimethyl-3-cyclopenten-1-yl)-2-pentanol (origin, Givaudan SA, Vernier, Switzerland);
- 10 - Group 3: damascones, Neobutenone[®] (1-(5,5-dimethyl-1-cyclohexen-1-yl)-4-penten-1-one, origin: Firmenich SA, Geneva, Switzerland), nectalactone ((1'R)-2-[2-(4'-methyl-3'-cyclohexen-1'-yl)propyl]cyclopentanone), alpha-ionone, beta-ionone, damascenone, Dynascone[®] (mixture of 1-(5,5-dimethyl-1-cyclohexen-1-yl)-4-penten-1-one and 1-(3,3-dimethyl-1-cyclohexen-1-yl)-4-penten-1-one, origin: Firmenich SA, Geneva, Switzerland), Dorinone[®] beta (1-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2-buten-1-one, origin: Firmenich SA, Geneva, Switzerland), Romandolide[®] ((1S,1'R)-[1-(3',3'-Dimethyl-1'-cyclohexyl)ethoxycarbonyl]methyl propanoate, origin: Firmenich SA, Geneva, Switzerland), 2-tert-butyl-1-cyclohexyl acetate (origin: International Flavors and Fragrances, USA), Limbanol[®] (1-(2,2,3,6-tetramethyl-cyclohexyl)-3-hexanol, origin: Firmenich SA, Geneva, Switzerland), trans-1-(2,2,6-trimethyl-1-cyclohexyl)-3-hexanol (origin: Firmenich SA,
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- Geneva, Switzerland), (E)-3-methyl-4-(2,6,6-trimethyl-2-cyclohexen-1-yl)-3-buten-2-one, terpenyl isobutyrate, Lorysia[®] (4-(1,1-dimethylethyl)-1-cyclohexyl acetate, origin: Firmenich SA, Geneva, Switzerland), 8-methoxy-1-p-menthene, Helvetolide[®] ((1S,1'R)-2-[1-(3',3'-dimethyl-1'-cyclohexyl) ethoxy]-2-methylpropyl propanoate, origin: Firmenich SA, Geneva, Switzerland), para tert-butylcyclohexanone, menthenethiol, 1-methyl-4-(4-methyl-3-pentenyl)-3-cyclohexene-1-carbaldehyde, allyl cyclohexylpropionate, cyclohexyl salicylate, 2-methoxy-4-methylphenyl methyl carbonate, ethyl 2-methoxy-4-methylphenyl carbonate, 4-ethyl-2-methoxyphenyl methyl carbonate;
- 5 - Group 4: Methyl cedryl ketone (origin: International Flavors and Fragrances, USA), Verdylate, vetyverol, vetyverone, 1-(octahydro-2,3,8,8-tetramethyl-2-naphthalenyl)-1-ethanone (origin: International Flavors and Fragrances, USA), (5RS,9RS,10SR)-2,6,9,10-tetramethyl-1-oxaspiro[4.5]deca-3,6-diene and the (5RS,9SR,10RS) isomer, 6-ethyl-2,10,10-trimethyl-1-oxaspiro[4.5]deca-3,6-diene, 1,2,3,5,6,7-hexahydro-1,1,2,3,3-pentamethyl-4-indenone (origin: International Flavors and Fragrances, USA), Hivernal[®] (a mixture of 3-
- 10 (3,3-dimethyl-5-indanyl)propanal and 3-(1,1-dimethyl-5-indanyl)propanal, origin: Firmenich SA, Geneva, Switzerland), Rhubofix[®] (3',4-dimethyl-tricyclo[6.2.1.0(2,7)]undec-4-ene-9-spiro-2'-oxirane, origin: Firmenich SA, Geneva, Switzerland), 9/10-ethyldiene-3-oxatricyclo[6.2.1.0(2,7)]undecane, Polywood[®] (perhydro-5,5,8A-trimethyl-2-naphthalenyl acetate, origin: Firmenich SA, Geneva, Switzerland), octalynol, Cetalo[®] (dodecahydro-
- 15 3a,6,6,9a-tetramethyl-naphtho[2,1-b]furan, origin: Firmenich SA, Geneva, Switzerland), tricyclo[5.2.1.0(2,6)]dec-3-en-8-yl acetate and tricyclo[5.2.1.0(2,6)]dec-4-en-8-yl acetate as well as tricyclo[5.2.1.0(2,6)]dec-3-en-8-yl propanoate and tricyclo[5.2.1.0(2,6)]dec-4-en-8-yl propanoate, (+)-(1S,2S,3S)-2,6,6-trimethyl-bicyclo[3.1.1]heptane-3-spiro-2'-cyclohexen-4'-one;
- 20 - Group 5: camphor, borneol, isobornyl acetate, 8-isopropyl-6-methyl-bicyclo[2.2.2]oct-5-ene-2-carbaldehyde, camphopinene, cedramber (8-methoxy-2,6,6,8-tetramethyl-tricyclo[5.3.1.0(1,5)]undecane, origin: Firmenich SA, Geneva, Switzerland), cedrene, cedrenol, cedrol, Florex[®] (mixture of 9-ethylidene-3-oxatricyclo[6.2.1.0(2,7)]undecan-4-one and 10-ethylidene-3-oxatricyclo[6.2.1.0(2,7)]undecan-4-one, origin: Firmenich SA, Geneva,
- 25 Switzerland), 3-methoxy-7,7-dimethyl-10-methylene-bicyclo[4.3.1]decane (origin: Firmenich SA, Geneva, Switzerland);
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- Group 6: Cedroxyde[®] (trimethyl-13-oxabicyclo-[10.1.0]-trideca-4,8-diene, origin: Firmenich SA, Geneva, Switzerland), Ambrettolide LG ((E)-9-hexadecen-16-olide, origin: Firmenich SA, Geneva, Switzerland), Habanolide[®] (pentadecenolide, origin: Firmenich SA, Geneva, Switzerland), muscenone (3-methyl-(4/5)-cyclopentadecenone, origin: Firmenich SA, Geneva, Switzerland), muscone (origin: Firmenich SA, Geneva, Switzerland), Exaltolide[®] (pentadecanolide, origin: Firmenich SA, Geneva, Switzerland), Exaltone[®] (cyclopentadecanone, origin: Firmenich SA, Geneva, Switzerland), (1-ethoxyethoxy)cyclododecane (origin: Firmenich SA, Geneva, Switzerland), Astrotone, 4,8-cyclododecadien-1-one;
- Group 7: Lilial[®] (origin: Givaudan SA, Vernier, Switzerland), rosinol.

Preferably, the perfume comprises at least 30%, preferably at least 50%, more preferably at least 60% of ingredients selected from Groups 1 to 7, as defined above. More preferably said perfume comprises at least 30%, preferably at least 50% of ingredients from Groups 3 to 7, as defined above. Most preferably said perfume comprises at least 30%, preferably at least 50% of ingredients from Groups 3, 4, 6 or 7, as defined above.

According to another preferred embodiment, the perfume comprises at least 30%, preferably at least 50%, more preferably at least 60% of ingredients having a logP above 3, preferably above 3.5 and even more preferably above 3.75.

Preferably, the perfume used in the invention contains less than 10% of its own weight of primary alcohols, less than 15% of its own weight of secondary alcohols and less than 20% of its own weight of tertiary alcohols. Advantageously, the perfume used in the invention does not contain any primary alcohols and contains less than 15% of secondary and tertiary alcohols.

According to an embodiment, the oil phase (or the oil-based core) comprises:

- 25-100wt% of a perfume oil comprising at least 15wt% of high impact perfume raw materials having a Log T<-4, and
- 0-75wt% of a density balancing material having a density greater than 1.07 g/cm³.

“*High impact perfume raw materials*” should be understood as perfume raw materials having a LogT<-4. The odor threshold concentration of a chemical compound is determined in part by its shape, polarity, partial charges and molecular mass. For convenience, the threshold concentration is presented as the common logarithm of the threshold concentration, i.e., Log [Threshold] (“LogT”).

A “*density balancing material*” should be understood as a material having a density greater than 1.07 g/cm³ and having preferably low or no odor.

The odor threshold concentration of a perfuming compound is determined by using a gas chromatograph (“GC”). Specifically, the gas chromatograph is calibrated to determine the exact volume of the perfume oil ingredient injected by the syringe, the precise split ratio, and the hydrocarbon response using a hydrocarbon standard of known concentration and chain-length distribution. The air flow rate is accurately measured and, assuming the duration of a human inhalation to last 12 seconds, the sampled volume is calculated. Since the precise concentration at the detector at any point in time is known, the mass per volume inhaled is known and hence the concentration of the perfuming compound. To determine the threshold concentration, solutions are delivered to the sniff port at the back-calculated concentration. A panelist sniffs the GC effluent and identifies the retention time when odor is noticed. The average across all panelists determines the odor threshold concentration of the perfuming compound. The determination of odor threshold is described in more detail in C. Vuilleumier et al., Multidimensional Visualization of Physical and Perceptual Data Leading to a Creative Approach in Fragrance Development, Perfume & Flavorist, Vol. 33, September,, 2008, pages 54-61.

The nature of high impact perfume raw materials having a Log T<-4 and density balancing material having a density greater than 1.07 g/cm³ are described in WO2018115250, the content of which are included by reference.

According to an embodiment, the high impact perfume raw materials having a Log T<-4 are selected from the list in Table A below.

Table A: high impact perfume raw materials having a Log T<-4

Perfume raw materials (Log T<-4)
(+)-1-METHOXY-3-HEXANETHIOL
4-(4-HYDROXY-1-PHENYL)-2-BUTANONE
(+)-2-(4-METHYL-3-CYCLOHEXEN-1-YL)-2-PROPANETHIOL
2-METHOXY-4-(1-PROPENYL)-1-PHENYL ACETATE
PYRAZOBUTYLE
3-PROPYLPHENOL
1-(3-METHYL-1-BENZOFURAN-2-YL)ETHANONE
2-(3-PHENYLPROPYL)PYRIDINE
1-(3,3-DIMETHYL-1-CYCLOHEXEN-1-YL)-4-PENTEN-1-ONE (A)

+ 1-(5,5-DIMETHYL-1-CYCLOHEXEN-1-YL)-4-PENTEN-1-ONE (B)
1-(5,5-DIMETHYL-1-CYCLOHEXEN-1-YL)-4-PENTEN-1-ONE
(3RS,3ARS,6SR,7ASR)-PERHYDRO-3,6-DIMETHYL-BENZO[B]FURAN-2-ONE (A) + (3SR,3ARS,6SR,7ASR)-PERHYDRO-3,6-DIMETHYL-BENZO[B]FURAN-2-ONE (B)
(+)-1-(5-ETHYL-5-METHYL-1-CYCLOHEXEN-1-YL)-4-PENTEN-1-ONE
(1'S,3'R)-1-METHYL-2-[(1',2',2'-TRIMETHYLBICYCLO[3.1.0]HEX-3'-YL)METHYL]CYCLOPROPYL}METHANOL
(+)-3-MERCAPTOHEXYL ACETATE
(2E)-1-(2,6,6-TRIMETHYL-1,3-CYCLOHEXADIEN-1-YL)-2-BUTEN-1-ONE
7-METHYL-2H-1,5-BENZODIOXEPIN-3(4H)-ONE
(2E,6Z)-2,6-NONADIEN-1-OL
(4Z)-4-DODECENAL
(+)-4-HYDROXY-2,5-DIMETHYL-3(2H)-FURANONE
METHYL 2,4-DIHYDROXY-3,6-DIMETHYLBENZOATE
3-METHYLINDOLE
(+)-PERHYDRO-4ALPHA,8ABETA-DIMETHYL-4A-NAPHTHALENOL
PATCHOULOL
2-METHOXY-4-(1-PROPENYL)PHENOL
(+)-5,6-DIHYDRO-4-METHYL-2-PHENYL-2H-PYRAN (A) + TETRAHYDRO-4-METHYLENE-2-PHENYL-2H-PYRAN (B)
4-METHYLENE-2-PHENYLTETRAHYDRO-2H-PYRAN (A) + (+)-4-METHYL-2-PHENYL-3,6-DIHYDRO-2H-PYRAN (B)
4-HYDROXY-3-METHOXYBENZALDEHYDE
NONYLENIC ALDEHYDE
2-METHOXY-4-PROPYLPHENOL
(2Z)-3-METHYL-5-PHENYL-2-PENTENENITRILE (A) + (2E)-3-METHYL-5-PHENYL-2-PENTENENITRILE (B)
1-(SPIRO[4.5]DEC-6-EN-7-YL)-4-PENTEN-1-ONE (A) + 1-(SPIRO[4.5]DEC-7-EN-7-YL)-4-PENTEN-1-ONE (B)
2-METHOXYNAPHTHALENE
(-)-(3AR,5AS,9AS,9BR)-3A,6,6,9A-TETRAMETHYLDODECAHYDRONAPHTHO[2,1-B]FURAN
5-NONANOLIDE
(3AR,5AS,9AS,9BR)-3A,6,6,9A-TETRAMETHYLDODECAHYDRONAPHTHO[2,1-B]FURAN
7-ISOPROPYL-2H,4H-1,5-BENZODIOXEPIN-3-ONE
COUMARIN
4-METHYLPHENYL ISOBUTYRATE
(2E)-1-(2,6,6-TRIMETHYL-1,3-CYCLOHEXADIEN-1-YL)-2-BUTEN-1-ONE

BETA,2,2,3-TETRAMETHYL-DELTA-METHYLENE-3-CYCLOPENTENE-1-BUTANOL
DELTA DAMASCONONE ((2E)-1-[(1R,2SR)-2,6,6-TRIMETHYL-3-CYCLOHEXEN-1-YL]-2-BUTEN-1-ONE)
(+)-3,6-DIHYDRO-4,6-DIMETHYL-2-PHENYL-2H-PYRAN
ANISALDEHYDE
PARACRESOL
3-ETHOXY-4-HYDROXYBENZALDEHYDE
METHYL 2-AMINO BENZOATE
ETHYL METHYLPHENYLGLYCIDATE
OCTALACTONE G
ETHYL 3-PHENYL-2-PROPENOATE
(-)-(2E)-2-ETHYL-4-[(1R)-2,2,3-TRIMETHYL-3-CYCLOPENTEN-1-YL]-2-BUTEN-1-OL
PARACRESYL ACETATE
DODECALACTONE
TRICYCLONE
(+)-(3R,5Z)-3-METHYL-5-CYCLOPENTADECEN-1-ONE
UNDECALACTONE
(1R,4R)-8-MERCAPTO-3-P-MENTHANONE
(3S,3AS,6R,7AR)-3,6-DIMETHYLHEXAHYDRO-1-BENZOFURAN-2(3H)-ONE
BÉTA IONONE
(+)-6-PENTYLTETRAHYDRO-2H-PYRAN-2-ONE
(3E,5Z)-1,3,5-UNDECATRIENE
10-UNDECENAL (A) + (9E)-9-UNDECENAL (B) + (9Z)-9-UNDECENAL (C)
(Z)-4-DECENAL
(+)-ETHYL 2-METHYLPENTANOATE
1,2-DIALLYLDISULFANE
(2Z)-2-TRIDECENENITRILE (A) + (3Z)-3-TRIDECENENITRILE (B) + (3E)-3-TRIDECENENITRILE (C) + (2E)-2-TRIDECENENITRILE (D)
(+)-2-ETHYL-4,4-DIMETHYL-1,3-OXATHIANE
(+)-(3R,5Z)-3-METHYL-5-CYCLOPENTADECEN-1-ONE
3-(4-TERT-BUTYLPHENYL)PROPANAL
ALLYL (CYCLOHEXYLOXY)ACETATE
METHYLNAPHTHYLKETONE
(+)-(4E)-3-METHYL-4-CYCLOPENTADECEN-1-ONE (A) + (+)-(5E)-3-METHYL-5-CYCLOPENTADECEN-1-ONE (B) + (+)-(5Z)-3-METHYL-5-CYCLOPENTADECEN-1-ONE (C)
CYCLOPROPYLMETHYL (3Z)-3-HEXENOATE (A) +

CYCLOPROPYLMETHYL (3E)-3-HEXENOATE (B)
(4E)-4-METHYL-5-(4-METHYLPHENYL)-4-PENTENAL
(+)-1-(5-PROPYL-1,3-BENZODIOXOL-2-YL)ETHANONE
4-METHYL-2-PENTYLPYRIDINE
(+)-(E)-3-METHYL-4-(2,6,6-TRIMETHYL-2-CYCLOHEXEN-1-YL)-3-BUTEN-2-ONE
(3ARS,5ASR,9ASR,9BRS)-3A,6,6,9A-TETRAMETHYLDODECAHYDRONAPHTHO[2,1-B]FURAN
(2S,5R)-5-METHYL-2-(2-PROPANYL)CYCLOHEXANONE OXIME
6-HEXYLTETRAHYDRO-2H-PYRAN-2-ONE
(+)-3-(3-ISOPROPYL-1-PHENYL)BUTANAL
METHYL 2-((1RS,2RS)-3-OXO-2-PENTYLCYCLOPENTYL)ACETATE (A) + METHYL 2-((1RS,2SR)-3-OXO-2-PENTYLCYCLOPENTYL)ACETATE (B)
1-(2,6,6-TRIMETHYL-1-CYCLOHEX-2-ENYL)PENT-1-EN-3-ONE
INDOL
7-PROPYL-2H,4H-1,5-BENZODIOXEPIN-3-ONE
ETHYL PRALINE
(4-METHYLPHENOXY)ACETALDEHYDE
ETHYL TRICYCLO[5.2.1.0.(2,6)]DECANE-2-CARBOXYLATE
(+)-(1'S,2S,E)-3,3-DIMETHYL-5-(2',2',3'-TRIMETHYL-3'-CYCLOPENTEN-1'-YL)-4-PENTEN-2-OL
(2R,4E)-3,3-DIMETHYL-5-[(1R)-2,2,3-TRIMETHYL-3-CYCLOPENTEN-1-YL]-4-PENTEN-2-OL (A) + (2S,4E)-3,3-DIMETHYL-5-[(1R)-2,2,3-TRIMETHYL-3-CYCLOPENTEN-1-YL]-4-PENTEN-2-OL (B)
8-ISOPROPYL-6-METHYL-BICYCLO[2.2.2]OCT-5-ENE-2-CARBALDEHYDE
METHYLNONYLACETALDEHYDE
4-FORMYL-2-METHOXYPHENYL 2-METHYLPROPANOATE
(E)-4-DECENAL
(+)-2-ETHYL-4-(2,2,3-TRIMETHYL-3-CYCLOPENTEN-1-YL)-2-BUTEN-1-OL
(1R,5R)-4,7,7-TRIMETHYL-6-THIABICYCLO[3.2.1]OCT-3-ENE (A) + (1R,4R,5R)-4,7,7-TRIMETHYL-6-THIABICYCLO[3.2.1]OCTANE (B)
(-)-(3R)-3,7-DIMETHYL-1,6-OCTADIEN-3-OL
(E)-3-PHENYL-2-PROPENENITRILE
4-METHOXYBENZYL ACETATE
(E)-3-METHYL-5-(2,2,3-TRIMETHYL-3-CYCLOPENTEN-1-YL)-4-PENTEN-2-OL
ALLYL (3-METHYLBUTOXY)ACETATE (A) + (+)-ALLYL (2-METHYLBUTOXY)ACETATE
(+)-(2E)-1-(2,6,6-TRIMETHYL-2-CYCLOHEXEN-1-YL)-2-BUTEN-

1-ONE
(1E)-1-(2,6,6-TRIMETHYL-1-CYCLOHEXEN-1-YL)-1-PENTEN-3-ONE

According to an embodiment, perfume raw materials having a Log T<-4 are chosen in the group consisting of aldehydes, ketones, alcohols, phenols, esters lactones, ethers, epoxydes, nitriles and mixtures thereof.

- 5 According to an embodiment, perfume raw materials having a Log T<-4 comprise at least one compound chosen in the group consisting of alcohols, phenols, esters lactones, ethers, epoxydes, nitriles and mixtures thereof, preferably in amount comprised between 20 and 70% by weight based on the total weight of the perfume raw materials having a Log T<-4.

10 According to an embodiment, perfume raw materials having a Log T<-4 comprise between 20 and 70% by weight of aldehydes, ketones, and mixtures thereof based on the total weight of the perfume raw materials having a Log T<-4.

The remaining perfume raw materials contained in the oil phase (or the oil-based core) may have therefore a Log T>-4.

15 Non limiting examples of perfume raw materials having a Log T>-4 are listed in table B below.

Table B: perfume raw materials having a Log T>-4

Perfume raw materials (Log T>-4)
ETHYL 2-METHYLBUTYRATE
(E)-3-PHENYL-2-PROPENYL ACETATE
(+)-8-SEC-BUTYLQUINOLINE (A) + (+)-6-SEC-BUTYLQUINOLINE
(+)-3-(1,3-BENZODIOXOL-5-YL)-2-METHYLPROPANAL
VERDYLE PROPIONATE
1-(OCTAHYDRO-2,3,8,8-TETRAMETHYL-2-NAPHTALENYL)-1-ETHANONE
METHYL 2-((1RS,2RS)-3-OXO-2-PENTYLCYCLOPENTYL)ACETATE
(+)-(E)-4-METHYL-3-DECEN-5-OL
2,4-DIMETHYL-3-CYCLOHEXENE-1-

CARBALDEHYDE
1,3,3-TRIMETHYL-2- OXABICYCLO[2.2.2]OCTANE
TETRAHYDRO-4-METHYL-2-(2- METHYL-1-PROPENYL)-2H-PYRAN
ALDEHYDE C 12
1-OXA-12-CYCLOHEXADECEN-2- ONE (A) + 1-OXA-13- CYCLOHEXADECEN-2-ONE (B)
(+)-3-(4-ISOPROPYLPHENYL)-2- METHYLPROPANAL
ALDEHYDE C 11 LENIQUE
(+)-2,6-DIMETHYL-7-OCTEN-2-OL
(+)-2,6-DIMETHYL-7-OCTEN-2-OL
ALLYL 3- CYCLOHEXYLPROPANOATE
(Z)-3-HEXENYL ACETATE
(2RS,5SR)-5-METHYL-2-(2- PROPANYL)CYCLOHEXANONE (A) + (2RS,5RS)-5-METHYL-2-(2- PROPANYL)CYCLOHEXANONE (B)
ALLYL HEPTANOATE
(1RS,2RS)-2-(2-METHYL-2- PROPANYL)CYCLOHEXYL ACETATE (A) + (1RS,2SR)-2-(2-METHYL-2- PROPANYL)CYCLOHEXYL ACETATE (B)
1,1-DIMETHYL-2-PHENYLETHYL BUTYRATE
GERANYL ACETATE (A) + NERYL ACETATE (B)
(+)-1-PHENYLETHYL ACETATE
1,1-DIMETHYL-2-PHENYLETHYL ACETATE
3-METHYL-2-BUTENYL ACETATE
ETHYL 3-OXOBUTANOATE (A) <=> (2Z)-ETHYL 3-HYDROXY-2- BUTENOATE (B)
8-P-MENTHANOL
8-P-MENTHANYL ACETATE (A) + 1- P-MENTHANYL ACETATE (B)
(+)-2-(4-METHYL-3-CYCLOHEXEN-1- YL)-2-PROPANYL ACETATE
(+)-2-METHYLBUTYL BUTANOATE
2-[(1S)-1-[(1R)-3,3-

DIMETHYLCYCLOHEXYL]ETHOXY}- 2-OXOETHYL PROPIONATE
3,5,6-TRIMETHYL-3-CYCLOHEXENE- 1-CARBALDEHYDE (A) + 2,4,6- TRIMETHYL-3-CYCLOHEXENE-1- CARBALDEHYDE (B)
2-CYCLOHEXYLETHYL ACETATE
ALDEHYDE C 8
ETHYL BUTANOATE
(+)-(3E)-4-(2,6,6-TRIMETHYL-2- CYCLOHEXEN-1-YL)-3-BUTEN-2- ONE (A) + (3E)-4-(2,6,6-TRIMETHYL- 1-CYCLOHEXEN-1-YL)-3-BUTEN-2- ONE (B);
1-[(1R,6SR)-2,2,6- TRIMETHYLCYCLOHEXYL]-3- HEXANOL
1,3,3-TRIMETHYL-2- OXABICYCLO[2.2.2]OCTANE
1,3,3-TRIMETHYL-2- OXABICYCLO[2.2.2]OCTANE
ETHYL HEXANOATE
UNDECANAL
ALDEHYDE C 10
2-PHENYLETHYL ACETATE
(1S,2S,4S)-1,7,7- TRIMETHYLBICYCLO[2.2.1]HEPTAN- 2-OL (A) + (1S,2R,4S)-1,7,7- TRIMETHYLBICYCLO[2.2.1]HEPTAN- 2-OL (B)
(+)-3,7-DIMETHYL-3-OCTANOL
1-METHYL-4-(2- PROPANYLIDENE)CYCLOHEXENE
(+)-(R)-4-(2-METHOXYPROPAN-2- YL)-1-METHYLCYCLOHEX-1-ENE
VERDYL ACETATE
(3R)-1-[(1R,6S)-2,2,6- TRIMETHYLCYCLOHEXYL]-3- HEXANOL (A) + (3S)-1-[(1R,6S)-2,2,6- TRIMETHYLCYCLOHEXYL]-3- HEXANOL (B) + (3R)-1-[(1S,6S)-2,2,6- TRIMETHYLCYCLOHEXYL]-3- HEXANOL (C)

(+)-(1S,1'R)-2-[1-(3',3'-DIMETHYL-1'-CYCLOHEXYL)ETHOXY]-2-METHYLPROPYL PROPANOATE

According to an embodiment, the oil-based core comprises 2-75wt% of a density balancing material having a density greater than 1.07 g/cm³ and 25-98wt% of a perfume oil comprising at least 15wt% of high impact perfume raw materials having a Log T<-4.

5 The density of a component is defined as the ratio between its mass and its volume (g/cm³).

Several methods are available to determine the density of a component.

One may refer for example to the ISO 298:1998 method to measure d20 densities of essential oils.

10 According to an embodiment, the density balancing material is chosen in the group consisting of benzyl salicylate, benzyl benzoate, cyclohexyl salicylate, benzyl phenylacetate, phenylethyl phenoxyacetate, triacetin, methyl and ethyl salicylate, benzyl cinnamate, and mixtures thereof.

15 According to a particular embodiment, the density balancing material is chosen in the group consisting of benzyl salicylate, benzyl benzoate, cyclohexyl salicylate and mixtures thereof.

By "flavour ingredient or composition" it is meant here a flavouring ingredient or a mixture of flavouring ingredients, solvent or adjuvants of current use for the preparation of a flavouring formulation, i.e. a particular mixture of ingredients which is intended to be added to an edible composition or chewable product to impart, improve or modify its organoleptic properties, in particular its flavour and/or taste. Taste modulator as also encompassed in said definition. Flavouring ingredients are well known to a skilled person in the art and their nature does not warrant a detailed description here, which in any case would not be exhaustive, the skilled flavourist being able to select them on the basis of his general knowledge and according to the intended use or application and the organoleptic effect it is desired to achieve. Many of these flavouring ingredients are listed in reference texts such as in the book by S. Arctander, Perfume and Flavor Chemicals, 1969, Montclair, N.J., USA, or its more recent versions, or in other works of similar nature such as Fenaroli's Handbook of Flavor Ingredients, 1975, CRC Press or Synthetic Food Adjuncts, 1947, by M.B. Jacobs, can Nostrand Co., Inc. Solvents and

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adjuvants or current use for the preparation of a flavouring formulation are also well known in the art.

In a particular embodiment, the flavour is selected from the group consisting of terpenic flavours including citrus and mint oil, and sulfury flavours.

5 According to a particular embodiment, the hydrophobic material is free of any active ingredient (such as perfume). According to this particular embodiment, it comprises, preferably consists of hydrophobic solvents, preferably chosen in the group consisting of isopropyl myristate, tryglycerides (e.g. Neobee® MCT oil, vegetable oils), D-limonene, silicone oil, mineral oil, and mixtures thereof with optionally hydrophilic solvents preferably chosen in the
10 group consisting of 1,4 butanediol, benzyl alcohol, triethyl citrate, triacetin, benzyl acetate, ethyl acetate, propylene glycol (1,2-propanediol), 1,3-Propanediol, dipropylene glycol, glycerol, glycol ethers and mixtures thereof .

 According to any one of the invention's embodiment, the oil represents between about
15 10% and 60% w/w, or even between 20% and 50% w/w, by weight, relative to the total weight of the dispersion.

 According to the invention, the aqueous phase comprises a "globular"protein.

 By "globular"protein, it should be understood a spherical protein characterized by a tertiary structure in the native state, and able to unfold and aggregate under the action of heat,
20 pressure or specific chemicals.

 As non-limiting examples of globular protein that can be used in the invention, one may cite whey protein, beta-lactoglobulin, ovalbumine, bovine serum albumin, vegetable proteins, and mixtures thereof.

 According to a particular embodiment, the protein is whey protein.

25 The weight ratio between the oil phase and the protein is preferably comprised between 1 and 10, more preferably between 2 and 4.

 The protein in the aqueous solution is used as an emulsifier and allows the stabilization of the oil droplets therein. The mean droplet size is preferably greater than 10 microns, preferably comprised between 10 and 500 microns, preferably between 15 and 500 microns, more
30 preferably between 20 and 500 microns.

The emulsion may be prepared by high shear mixing and adjusted to the desired droplet size. The droplet size can be checked with light scattering measurements or microscopy. This procedure does not require a more detailed description here as it is well known to a skilled person in the art.

5 According to a particular embodiment, before the emulsion formation, the aqueous phase comprising the protein is formerly heated (at a temperature slightly below or about to T_{den} (denaturation temperature) and for a short period of time) to initiate the denaturation of the protein. According to this embodiment, the aqueous solution may be heated between 75°C and 80°C, preferably during 5 and 15 minutes and then cooled down before the mixing with the oil
10 phase. This enables the display of hydrophobic moieties and better adsorption at the O/W interface.

Step b) adding an aqueous solution comprising a polysaccharide into the oil-in-water emulsion

15 In step b) of the process, an aqueous solution of a polysaccharide is added in the oil-in-water emulsion stabilized with the protein.

Polysaccharide that can be used in the present invention may be pectin, carrageenans, alginate, and mixtures thereof.

According to a particular embodiment, the polysaccharide is pectin.

20 Pectins are polysaccharides extracted from plants and containing methoxyl groups on their sugar moieties in the native form. They are characterized by a esterification degree (DE). In the present invention, the pectin used for the complex formation with the protein is preferably a high methoxy (ie high DE) pectin (HMP). The high methoxy pectin is particularly useful to avoid the microcapsules aggregation.

25 Without being bound by any theory, the inventors are of the opinion that, when the polysaccharide is added into the oil-in-water emulsion of step a), the polysaccharide interacts with the protein to form protein/polysaccharide complexes at the oil-water interface in which at least one part of the added polysaccharide is adsorbed onto the protein.

Those protein/polysaccharide complexes limit a bulk aggregation of the microcapsules during the denaturation and also improve the shell rigidity once formed.

30 The weight ratio between the protein and the polysaccharide is preferably comprised between 1 and 10, more preferably comprised between 3 and 8.

To improve the aggregation of the protein to form the membrane, the process of the invention may comprise a further step consisting in adding a salt solution, preferably a calcium solution in the emulsion obtained in step a) and/ or in the mixture obtained in step b).

According to this embodiment, the weight ratio between the protein and calcium is preferably comprised between 1 and 10, more preferably between 2 and 4.

After step b), the pH is preferably comprised between 4 and 6, more preferably between 5 and 5.5.

Step c) Applying sufficient conditions to induce the denaturation of the protein so as to form core-shell microcapsules in the form of a slurry

Methods for denaturation of proteins are well-known from the person skilled in the art. As non-limiting examples, according to the invention, denaturation of proteins can be induced by heat, by high pressure treatment, by combinations of heat and pressure treatments, by addition of alcohols, by addition of acids or bases, by addition of salts including heavy metal salts (e.g. silver nitrate), or by chemical denaturation with chaotropic agents such as urea, guanidinium chloride or sodium dodecyl sulfate or disulfide bond reducers, such as 2-mercaptoethanol or dithiothreitol.

According to an embodiment, in step c) of the process, a heating step is carried out to denature the protein and induce the aggregation of the protein/polysaccharides complexes at the oil-water interface. A core-shell capsule slurry is obtained.

The heating step can be carried out at a temperature T_{den} (denaturation temperature of the protein), preferably comprised between 50°C and 100°C, more preferably between 80°C and 100°C. The duration of the heating step will depend on the heating temperature. Typically, the duration of the heating step is comprised between 10 and 60 minutes.

According to the nature of the protein, the person skilled in the art will be able to find a suitable temperature to induce the denaturation of said protein.

As non-limiting examples, the denaturation temperature T_{den} of:

- whey protein is comprised between 70 and 90°C
- soy protein is comprised between 70 and 90°C
- bovine serum albumin is comprised between 50 and 82°C
- ovalbumin is comprised between 68 and 80°C

- potato protein is comprised between 50 and 90°C.

The heating step is preferably performed at a pH comprised between 4 and 6, more preferably between 5 and 5.5.

5 Optional cross-linking step(s):

Depending to the targeted applications, it could be interesting to improve the barrier properties of the biopolymer membrane.

One may use enzymatic and/or chemical cross-linker(s) to densify the membrane of the microcapsules.

- 10 According to an embodiment, a crosslinker, preferably chosen in the group consisting of transglutaminase, glutaraldehyde, genipin, and mixtures thereof is added in the mixture obtained in step b) and/or in the mixture obtained in step c).

According to this embodiment, the cross-linker is used in an amount comprised between 0.1 and 2% based on the microcapsule slurry.

- 15 According to another embodiment, the process comprises the steps of:

- a) dispersing an oil phase comprising a hydrophobic material, preferably a flavor or a perfume, and a polyfunctional monomer, into an aqueous phase comprising a protein to form an oil-in-water emulsion;
- b) adding an aqueous solution comprising a polysaccharide into the oil-in-water
20 emulsion;
- c) applying conditions sufficient to induce interfacial polymerization of the monomer to form an inner shell; and
- d) applying sufficient conditions, preferably by heating the mixture obtained in step c) at a temperature T_{den} to induce the denaturation of the protein so as to form an outer
25 shell.

According to this embodiment, a polyfunctional monomer is further added into the oil phase in addition to the hydrophobic material.

- 30 By “polyfunctional polymer”, it is meant a molecule that, as unit, reacts or binds chemically to form a polymer or supramolecular polymer. The polyfunctional polymer of the invention has at least two functions capable of forming a microcapsule shell.

The polyfunctional monomer may be chosen in the group consisting of at least one polyisocyanate, poly maleic anhydride, poly acyl chloride, polyepoxide, acrylate monomers and polyalkoxysilane.

The polyfunctional monomer used in the process according to the invention is present in amounts representing from 0.1 to 15%, preferably from 0.5 to 10% and more preferably from 0.5 to 6%, and even more preferably between 2 and 4% by weight of the oil phase.

According to a particular embodiment, the monomer added in step a) is at least one polyisocyanate having at least two isocyanate functional groups.

Suitable polyisocyanates used according to the invention include aromatic polyisocyanate, aliphatic polyisocyanate and mixtures thereof. Said polyisocyanate comprises at least 2, preferably at least 3 but may comprise up to 6, or even only 4, isocyanate functional groups. According to a particular embodiment, a triisocyanate (3 isocyanate functional groups) is used.

According to one embodiment, said polyisocyanate is an aromatic polyisocyanate.

The term "aromatic polyisocyanate" is meant here as encompassing any polyisocyanate comprising an aromatic moiety. Preferably, it comprises a phenyl, a toluyl, a xylyl, a naphthyl or a diphenyl moiety, more preferably a toluyl or a xylyl moiety. Preferred aromatic polyisocyanates are biurets, polyisocyanurates and trimethylol propane adducts of diisocyanates, more preferably comprising one of the above-cited specific aromatic moieties. More preferably, the aromatic polyisocyanate is a polyisocyanurate of toluene diisocyanate (commercially available from Bayer under the tradename Desmodur[®] RC), a trimethylol propane-adduct of toluene diisocyanate (commercially available from Bayer under the tradename Desmodur[®] L75), a trimethylol propane-adduct of xylylene diisocyanate (commercially available from Mitsui Chemicals under the tradename Takenate[®] D-110N). In a most preferred embodiment, the aromatic polyisocyanate is a trimethylol propane-adduct of xylylene diisocyanate.

According to another embodiment, said polyisocyanate is an aliphatic polyisocyanate. The term "aliphatic polyisocyanate" is defined as a polyisocyanate which does not comprise any aromatic moiety. Preferred aliphatic polyisocyanates are a trimer of hexamethylene diisocyanate, a trimer of isophorone diisocyanate, a trimethylol propane-adduct of hexamethylene diisocyanate (available from Mitsui Chemicals) or a biuret of hexamethylene diisocyanate (commercially available from Bayer under the tradename Desmodur[®] N 100), among which a biuret of hexamethylene diisocyanate is even more preferred.

According to another embodiment, the at least one polyisocyanate is in the form of a mixture of at least one aliphatic polyisocyanate and of at least one aromatic polyisocyanate, both comprising at least two or three isocyanate functional groups, such as a mixture of a biuret of hexamethylene diisocyanate with a trimethylol propane-adduct of xylylene diisocyanate, a mixture of a biuret of hexamethylene diisocyanate with a polyisocyanurate of toluene diisocyanate and a mixture of a biuret of hexamethylene diisocyanate with a trimethylol propane-adduct of toluene diisocyanate. Most preferably, it is a mixture of a biuret of hexamethylene diisocyanate with a trimethylol propane-adduct of xylylene diisocyanate. Preferably, when used as a mixture the molar ratio between the aliphatic polyisocyanate and the aromatic polyisocyanate is ranging from 80:20 to 10:90.

According to an embodiment, the at least one polyisocyanate used in the process of the invention is present in amounts representing from 0.1 to 15%, preferably from 0.5 to 10% and more preferably from 0.5 to 6%, and even more preferably between 2 and 4% by weight of the oil phase.

When a polyfunctional monomer is added in the oil phase, the process comprises a further step consisting in applying conditions sufficient to induce interfacial polymerization of the polyfunctional monomer to form an inner shell.

The inner shell of the microcapsules is the result of the interfacial polymerization between the polyfunctional monomer and the functional groups of the protein or between the polyfunctional monomer and water.

No specific action is required to induce interfacial polymerization. Preferably, the mixture obtained in step b) is maintained under stirring for 2 to 15 hours, preferably for 2 to 10 hours.

To increase the reaction kinetics, the stirring can be made at a pH comprised between 7 and 10 and/or at a temperature comprised between 50 and 70°C (which has to be lower than the denaturation temperature of the protein).

The nature of the inner shell depends on the nature of the monomer present in the oil phase. According to an embodiment, the inner shell is polyurea shell.

Optional outer coating

According to a particular embodiment of the invention, at the end of step c) one may also add to the invention's slurry a polymer selected from a non-ionic polysaccharide, a cationic polymer and mixtures thereof to form an outer coating to the microcapsules.

5 Non-ionic polysaccharide polymers are well known to a person skilled in the art and are described for instance in WO2012/007438 page 29, lines 1 to 25 and in WO2013/026657 page 2, lines 12 to 19 and page 4, lines 3 to 12. Preferred non-ionic polysaccharides are selected from the group consisting of locust bean gum, xyloglucan, guar gum, hydroxypropyl guar, hydroxypropyl cellulose and hydroxypropyl methyl cellulose.

10 Cationic polymers are well known to a person skilled in the art. Preferred cationic polymers have cationic charge densities of at least 0.5 meq/g, more preferably at least about 1.5 meq/g, but also preferably less than about 7 meq/g, more preferably less than about 6.2 meq/g. The cationic charge density of the cationic polymers may be determined by the Kjeldahl method as described in the US Pharmacopoeia under chemical tests for Nitrogen determination. The
15 preferred cationic polymers are chosen from those that contain units comprising primary, secondary, tertiary and/or quaternary amine groups that can either form part of the main polymer chain or can be borne by a side substituent directly connected thereto. The weight average (Mw) molecular weight of the cationic polymer is preferably between 10,000 and 3.5M Dalton, more preferably between 50,000 and 1.5M Dalton. According to a particular embodiment, one will use
20 cationic polymers based on acrylamide, methacrylamide, N-vinylpyrrolidone, quaternized N,N-dimethylaminomethacrylate, diallyldimethylammonium chloride, quaternized vinylimidazole (3-methyl-1-vinyl-1H-imidazol-3-ium chloride), vinylpyrrolidone, acrylamidopropyltrimonium chloride, cassia hydroxypropyltrimonium chloride, guar hydroxypropyltrimonium chloride or polygalactomannan 2-hydroxypropyltrimethylammonium chloride ether, starch
25 hydroxypropyltrimonium chloride and cellulose hydroxypropyltrimonium chloride. Preferably copolymers shall be selected from the group consisting of polyquaternium-5, polyquaternium-6, polyquaternium-7, polyquaternium-10, polyquaternium-11, polyquaternium-16, polyquaternium-22, polyquaternium-28, polyquaternium-43, polyquaternium-44, polyquaternium-46, cassia hydroxypropyltrimonium chloride, guar hydroxypropyltrimonium chloride or
30 polygalactomannan 2-hydroxypropyltrimethylammonium chloride ether, starch hydroxypropyltrimonium chloride and cellulose hydroxypropyltrimonium chloride. As specific

examples of commercially available products, one may cite Salcare[®] SC60 (cationic copolymer of acrylamidopropyltrimonium chloride and acrylamide, origin: BASF) or Luviquat[®], such as the PQ 11N, FC 550 or Style (polyquaternium-11 to 68 or quaternized copolymers of vinylpyrrolidone origin: BASF), or also the Jaguar[®] (C13S or C17, origin Rhodia).

5 According to any one of the above embodiments of the invention, there is added an amount of polymer described above comprised between about 0% and 5% w/w, or even between about 0.1% and 2% w/w, percentage being expressed on a w/w basis relative to the total weight of the slurry as obtained after step c). It is clearly understood by a person skilled in the art that only part of said added polymers will be incorporated into/deposited on the microcapsule shell.

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Multiple microcapsules system

According to an embodiment, the microcapsules of the invention (first microcapsule slurry) can be used in combination with a second microcapsules slurry.

Another object of the invention is a microcapsule delivery system comprising:

- 15 - the microcapsule slurry of the present invention as a first microcapsule slurry, and
 - a second microcapsule slurry, wherein the microcapsules contained in the first microcapsule slurry and the second microcapsule slurry differ in their hydrophobic material and/or their wall material and/or in their coating material.

As non-limiting examples, the nature of the polymeric shell of the second microcapsule slurry of the invention can vary. As non-limiting examples, the shell of the second microcapsules slurry can be aminoplast-based, polyurea-based or polyurethane-based. The shell of the second microcapsules slurry can also be hybrid, namely organic-inorganic such as a hybrid shell composed of at least two types of inorganic particles that are cross-linked, or yet a shell resulting from the hydrolysis and condensation reaction of a polyalkoxysilane macro-monomeric composition.

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According to an embodiment, the shell of the second microcapsules slurry comprises an aminoplast copolymer, such as melamine-formaldehyde or urea-formaldehyde or cross-linked melamine formaldehyde or melamine glyoxal.

According to another embodiment the shell of the second microcapsules slurry is
30 polyurea-based made from, for example but not limited to isocyanate-based monomers and amine-containing crosslinkers such as guanidine carbonate and/or guanazole. Preferred polyurea

microcapsules comprise a polyurea wall which is the reaction product of the polymerisation between at least one polyisocyanate comprising at least two isocyanate functional groups and at least one reactant selected from the group consisting of an amine (for example a water soluble guanidine salt and guanidine); a colloidal stabilizer or emulsifier; and an encapsulated perfume.

5 However, the use of an amine can be omitted. According to a particular embodiment the colloidal stabilizer includes an aqueous solution of between 0.1% and 0.4% of polyvinyl alcohol, between 0.6% and 1% of a cationic copolymer of vinylpyrrolidone and of a quaternized vinylimidazol (all percentages being defined by weight relative to the total weight of the colloidal stabilizer). According to another embodiment, the emulsifier is an anionic or
10 amphiphilic biopolymer preferably chosen from the group consisting of gum Arabic, soy protein, sodium caseinate, gelatin and mixtures thereof.

According to another embodiment, the shell of the second microcapsules slurry is polyurethane-based made from, for example but not limited to polyisocyanate and polyols, polyamide, polyester, etc.

15 The preparation of an aqueous dispersion/slurry of core-shell microcapsules is well known by a skilled person in the art. In one aspect, said microcapsule wall material may comprise any suitable resin and especially including melamine, glyoxal, polyurea, polyurethane, polyamide, polyester, etc. Suitable resins include the reaction product of an aldehyde and an amine, suitable aldehydes include, formaldehyde and glyoxal. Suitable amines include melamine,
20 urea, benzoguanamine, glycoluril, and mixtures thereof. Suitable melamines include, methylol melamine, methylated methylol melamine, imino melamine and mixtures thereof. Suitable ureas include, dimethylol urea, methylated dimethylol urea, urea-resorcinol, and mixtures thereof. Suitable materials for making may be obtained from one or more of the following companies Solutia Inc. (St Louis, Missouri U.S.A.), Cytec Industries (West Paterson, New Jersey U.S.A.),
25 Sigma-Aldrich (St. Louis, Missouri U.S.A.).

According to a particular embodiment, the second core-shell microcapsule is a formaldehyde-free capsule. A typical process for the preparation of aminoplast formaldehyde-free microcapsules slurry comprises the steps of 1) preparing an oligomeric composition comprising the reaction product of, or obtainable by reacting together

30 a) a polyamine component in the form of melamine or of a mixture of melamine and at least one C₁-C₄ compound comprising two NH₂ functional groups;

- b) an aldehyde component in the form of a mixture of glyoxal, a C₄₋₆ 2,2-dialkoxy-ethanal and optionally a glyoxalate, said mixture having a molar ratio glyoxal/C₄₋₆ 2,2-dialkoxy-ethanal comprised between 1/1 and 10/1; and
- c) a protic acid catalyst;
- 5 2) preparing an oil-in-water dispersion, wherein the droplet size is comprised between 1 and 600 μm, and comprising:
- i. an oil;
 - ii. a water medium
 - iii. at least an oligomeric composition as obtained in step 1;
 - 10 iv. at least a cross-linker selected amongst
- A) C₄-C₁₂ aromatic or aliphatic di- or tri-isocyanates and their biurets, triurets, trimers, trimethylol propane-adduct and mixtures thereof; and/or
- B) a di- or tri-oxiran compounds of formula
- A-(oxiran-2-ylmethyl)_n
- 15 wherein n stands for 2 or 3 and 1 represents a C₂-C₆ group optionally comprising from 2 to 6 nitrogen and/or oxygen atoms;
- v. optionally a C₁-C₄ compounds comprising two NH₂ functional groups;
- 3) Heating said dispersion;
- 4) Cooling said dispersion.
- 20 This process is described in more details in WO 2013/068255, the content of which is included by reference.
- According to another embodiment, the shell of the of the second microcapsules slurry is polyurea-or polyurethane-based. Examples of processes for the preparation of polyurea and polyurethane-based microcapsule slurry are for instance described in WO2007/004166, EP
- 25 2300146, EP2579976 the contents of which is also included by reference. Typically a process for the preparation of polyurea or polyurethane-based microcapsule slurry include the following steps:
- a) Dissolving at least one polyisocyanate having at least two isocyanate groups in an oil to form an oil phase;
 - 30 b) Preparing an aqueous solution of an emulsifier or colloidal stabilizer to form a water phase;

- c) Adding the oil phase to the water phase to form an oil-in-water dispersion, wherein the mean droplet size is comprised between 1 and 500 μm , preferably between 5 and 50 μm ;
- d) Applying conditions sufficient to induce interfacial polymerisation and form microcapsules in form of a slurry.

5

Process for preparing a microcapsule powder

Another object of the invention is a process for preparing a microcapsule powder comprising the steps as defined above and an additional step d) consisting of submitting the slurry obtained in step c) (after the heating step) to a drying, like spray-drying, to provide the microcapsules as such, i.e. in a powdery form. It is understood that any standard method known by a person skilled in the art to perform such drying is also applicable. In particular the slurry may be spray-dried preferably in the presence of a polymeric carrier material such as polyvinyl acetate, polyvinyl alcohol, dextrans, natural or modified starch, vegetable gums, pectins, xanthans, alginates, carragenans or cellulose derivatives to provide microcapsules in a powder form.

15

According to a particular embodiment, the carrier material contains free perfume oil which can be same or different from the perfume from the core of the microcapsules.

Microcapsule slurry/Microcapsule powder

20

Other objects of the invention are a microcapsule slurry or microcapsule powder comprising at least one microcapsule made of:

25

- an oil-based core comprising a hydrophobic material, and
- at least one shell comprising a protein and a polysaccharide, wherein the protein is preferably whey protein and wherein the polysaccharide is preferably pectin.

Definitions regarding the hydrophobic material, polysaccharide, globular protein, polyfunctional monomer are the same as described above for the process for preparing core-shell microcapsules slurry.

Another object of the invention is a microcapsule slurry comprising at least one microcapsules made of:

30

- an oil-based core comprising a hydrophobic material

- an inner shell made of a polymerized polyfunctional monomer and an outer shell made of a protein, preferably a globular protein and a polysaccharide.

According to an embodiment, the outer shell comprises pectin and whey protein and/or the inner shell comprises a polymerized polyisocyanate having at least two isocyanate groups.

The shell of the microcapsule of the invention is made of protein/polysaccharides complexes.

Microcapsule slurry and microcapsule powder obtainable by the processes above-described are also an object of the invention.

Consumer products

The microcapsules of the invention can be used for the preparation of perfuming or flavouring compositions which are also an object of the invention.

Flavored consumer products

The microcapsules of the invention when encapsulating a flavour, can be used in a great variety of edible end products. Consumer products susceptible of being flavoured by the microcapsules of the invention may include foods, beverages, pharmaceutical and the like. For example foodstuff base that could use the powdered microcapsules of the invention include

- Baked goods (e.g. bread, dry biscuits, cakes, other baked goods),
- Non-alcoholic beverages (e.g. carbonated soft drinks, bottled waters , sports/energy drinks , juice drinks, vegetable juices, vegetable juice preparations),
- Alcoholic beverages (e.g. beer and malt beverages, spirituous beverages),
- Instant beverages (e.g. instant vegetable drinks, powdered soft drinks, instant coffee and tea),
- Cereal products (e.g. breakfast cereals, pre-cooked ready-made rice products, rice flour products, millet and sorghum products, raw or pre-cooked noodles and pasta products),
- Milk products (e.g. fresh cheese, soft cheese, hard cheese, milk drinks, whey, butter, partially or wholly hydrolysed milk protein-containing products, fermented milk products, condensed milk and analogues),
- Dairy based products (e.g. fruit or flavored yoghurt, ice cream, fruit ices)
- Confectionary products (e.g. chewing gum, hard and soft candy)

- Chocolate and compound coatings
- Products based on fat and oil or emulsions thereof (e.g. mayonnaise, spreads, margarines, shortenings, remoulade, dressings, spice preparations),
- Spiced, marinated or processed fish products (e.g. fish sausage, surimi),
- 5 • Eggs or egg products (dried egg, egg white, egg yolk, custard),
- Desserts (e.g. gelatins and puddings)
- Products made of soya protein or other soya bean fractions (e.g. soya milk and products made therefrom, soya lecithin-containing preparations, fermented products such as tofu or tempeh or products manufactured therefrom, soya sauces),
- 10 • Vegetable preparations (e.g. ketchup, sauces, processed and reconstituted vegetables, dried vegetables, deep frozen vegetables, pre-cooked vegetables, vegetables pickled in vinegar, vegetable concentrates or pastes, cooked vegetables, potato preparations),
- Vegetarian meat replacer, vegetarian burger
- Spices or spice preparations (e.g. mustard preparations, horseradish preparations), spice
- 15 mixtures and, in particular seasonings which are used, for example, in the field of snacks.
- Snack articles (e.g. baked or fried potato crisps or potato dough products, bread dough products, extrudates based on maize, rice or ground nuts),
- Meat products (e.g. processed meat, poultry, beef, pork, ham, fresh sausage or raw meat preparations, spiced or marinated fresh meat or cured meat products, reformed meat),
- 20 • Ready dishes (e.g. instant noodles, rice, pasta, pizza, tortillas, wraps) and soups and broths (e.g. stock, savory cube, dried soups, instant soups, pre-cooked soups, retorted soups), sauces (instant sauces, dried sauces, ready-made sauces, gravies, sweet sauces).

Preferably, the microcapsules according to the invention shall be used in products selected from the group consisting of baked goods, instant beverages, cereal products, milk products, dairy-

25 based products, products based on fat and oil or emulsions thereof, desserts, vegetable preparations, vegetarian meat replacer, spices and seasonings, snacks, meat products, ready dishes, soups and broths and sauces.

Perfumed consumer products

The microcapsules of the invention can be used in combination with active ingredients.

30 An object of the invention is therefore a composition comprising:

- (i) microcapsules as defined above;

(ii) an active ingredient, preferably chosen in the group consisting of a cosmetic ingredient, skin caring ingredient, perfume ingredient, flavor ingredient, malodour counteracting ingredient, bactericide ingredient, fungicide ingredient, pharmaceutical or agrochemical ingredient, a sanitizing ingredient, an insect repellent or attractant, and mixtures thereof.

5 The microcapsules of the invention can also be added in different perfumed consumer products.

 In particular a perfuming composition comprising (i) microcapsules as defined above; (ii) at least one perfuming co-ingredient; and (iii) optionally a perfumery adjuvant, is another object of the invention.

10 By “perfuming co-ingredient” it is meant here a compound, which is used in a perfuming preparation or a composition to impart a hedonic effect and which is not a microcapsule as defined above. In other words such a co-ingredient, to be considered as being a perfuming one, must be recognized by a person skilled in the art as being able to impart or modify in a positive or pleasant way the odor of a composition, and not just as having an odor. The nature and type of
15 the perfuming co-ingredients present in the perfuming composition do not warrant a more detailed description here, which in any case would not be exhaustive, the skilled person being able to select them on the basis of his general knowledge and according to the intended use or application and the desired organoleptic effect. In general terms, these perfuming co-ingredients belong to chemical classes as varied as alcohols, lactones, aldehydes, ketones, esters, ethers,
20 acetates, nitriles, terpenoids, nitrogenous or sulphurous heterocyclic compounds and essential oils, and said perfuming co-ingredients can be of natural or synthetic origin. Many of these co-ingredients are in any case listed in reference texts such as the book by S. Arctander, Perfume and Flavor Chemicals, 1969, Montclair, New Jersey, USA, or its more recent versions, or in other works of a similar nature, as well as in the abundant patent literature in the field of
25 perfumery. It is also understood that said co-ingredients may also be compounds known to release in a controlled manner various types of perfuming compounds.

 By “perfumery adjuvant” we mean here an ingredient capable of imparting additional added benefit such as a color, a particular light resistance, chemical stability, etc. A detailed description of the nature and type of adjuvant commonly used in perfuming bases cannot be
30 exhaustive, but it has to be mentioned that said ingredients are well known to a person skilled in the art.

Preferably, the perfuming composition according to the invention comprises between 0.1 and 30 % by weight of microcapsules as defined above.

The invention's microcapsules can advantageously be used in many application fields and used in consumer products. Microcapsules can be used in liquid form applicable to liquid
5 consumer products as well as in powder form, applicable to powder consumer products.

In the case of microcapsules including a perfume oil-based core, the products of the invention, can in particular be of used in perfumed consumer products such as product belonging to fine fragrance or "functional" perfumery. Functional perfumery includes in particular personal-care products including hair-care, body cleansing, skin care, hygiene-care as well as
10 home-care products including laundry care and air care. Consequently, another object of the present invention consists of a perfumed consumer product comprising as a perfuming ingredient, the microcapsules defined above or a perfuming composition as defined above. The perfume element of said consumer product can be a combination of perfume microcapsules as defined above and free or non-encapsulated perfume, as well as other types of perfume microcapsule
15 than those here-disclosed.

In particular a liquid consumer product comprising:

- from 2 to 65% by weight, relative to the total weight of the consumer product, of at least one surfactant;
- water or a water-miscible hydrophilic organic solvent; and
- 20 - a perfuming composition or microcapsules as defined above, wherein the hydrophobic material comprises a perfume is another object of the invention.

Also a powder consumer product comprising

- from 2 to 65% by weight, relative to the total weight of the consumer product, of at least one surfactant; and
- 25 - a perfuming composition or microcapsules, wherein the hydrophobic material comprises a perfume as defined above is part of the invention.

According to a particular embodiment, the process for preparing the microcapsules comprised in the perfumed consumer product comprises a cross-linking step as defined above (chemically and/or enzymatically) to improve the stability in challenging bases comprising a
30 high amount of surfactants.

The invention's microcapsules can therefore be added as such or as part of an invention's perfuming composition in a perfumed consumer product.

For the sake of clarity, it has to be mentioned that, by "perfumed consumer product" it is meant a consumer product which is expected to deliver among different benefits a perfuming effect to the surface to which it is applied (e.g. skin, hair, textile, paper, or home surface) or in the air (air-freshener, deodorizer etc). In other words, a perfumed consumer product according to the invention is a manufactured product which comprises a functional formulation also referred to as "base", together with benefit agents, among which an effective amount of microcapsules according to the invention.

The nature and type of the other constituents of the perfumed consumer product do not warrant a more detailed description here, which in any case would not be exhaustive, the skilled person being able to select them on the basis of his general knowledge and according to the nature and the desired effect of said product. Base formulations of consumer products in which the microcapsules of the invention can be incorporated can be found in the abundant literature relative to such products. These formulations do not warrant a detailed description here which would in any case not be exhaustive. The person skilled in the art of formulating such consumer products is perfectly able to select the suitable components on the basis of his general knowledge and of the available literature.

Non-limiting examples of suitable perfumed consumer product can be a perfume, such as a fine perfume, a cologne, an after-shave lotion, a body-splash; a fabric care product, such as a liquid or solid detergent, tablets and pods, a fabric softener, a dryer sheet, a fabric refresher, an ironing water, or a bleach; a personal-care product, such as a hair-care product (e.g. a shampoo, hair conditioner, a colouring preparation or a hair spray), a cosmetic preparation (e.g. a vanishing cream, body lotion or a deodorant or antiperspirant), or a skin-care product (e.g. a perfumed soap, shower or bath mousse, body wash, oil or gel, bath salts, or a hygiene product); an air care product, such as an air freshener or a "ready to use" powdered air freshener; or a home care product, such all-purpose cleaners, liquid or power or tablet dishwashing products, toilet cleaners or products for cleaning various surfaces, for example sprays & wipes intended for the treatment / refreshment of textiles or hard surfaces (floors, tiles, stone-floors etc.); a hygiene product such as sanitary napkins, diapers, toilet paper.

Another object of the invention is a consumer product comprising:

- a personal care active base, and
 - microcapsules as defined above or the perfuming composition as defined above,
- wherein the consumer product is in the form of a personal care composition.

Personal care active base in which the microcapsules of the invention can be incorporated
5 can be found in the abundant literature relative to such products. These formulations do not warrant a detailed description here which would in any case not be exhaustive. The person skilled in the art of formulating such consumer products is perfectly able to select the suitable components on the basis of his general knowledge and of the available literature.

The personal care composition is preferably chosen in the group consisting of a hair-care product
10 (e.g. a shampoo, hair conditioner, a colouring preparation or a hair spray), a cosmetic preparation (e.g. a vanishing cream, body lotion or a deodorant or antiperspirant), a skin-care product (e.g. a perfumed soap, shower or bath mousse, body wash, oil or gel, bath salts, or a hygiene product), oral care product (toothpaste or mouthwash composition) or a fine fragrance product (e.g. Eau de Toilette - EdT).

15 Another object of the invention is a consumer product comprising:

- a home care or a fabric care active base, and
 - microcapsules as defined above or the perfuming composition as defined above,
- wherein the consumer product is in the form of a home care or a fabric care composition.

Home care or fabric care bases in which the microcapsules of the invention can be
20 incorporated can be found in the abundant literature relative to such products. These formulations do not warrant a detailed description here which would in any case not be exhaustive. The person skilled in the art of formulating such consumer products is perfectly able to select the suitable components on the basis of his general knowledge and of the available literature.

25 The home or fabric care composition is preferably chosen in the group consisting fabric softener, liquid detergent, powder detergent, liquid scent booster solid scent booster.

According to a particular embodiment, the consumer product is in the form of a fabric softener composition and comprises:

- between 85 and 99.9% of a fabric softener active base;
- 30 - between 0.1 to 15 wt%, more preferably between 0.2 and 5 wt% by weight of the microcapsule slurry of the invention.

The fabric softener active base may comprise cationic surfactants of quaternary ammonium, such as Diethyl ester dimethyl ammonium chloride (DEEDMAC), TEAQ (triethanolamine quat), HEQ (Hamburg esterquat), and mixtures thereof.

According to a particular embodiment, the consumer product is in the form of a perfuming composition comprising:

- 0.1 to 20% of microcapsules as defined previously,
- 0 to 40%, preferably 3-40% of perfume, and
- 40-90% of ethanol, by weight based on the total weight of the perfuming composition.

Preferably, the consumer product comprises from 0.1 to 15 wt%, more preferably between 0.2 and 5 wt% of the microcapsules of the present invention, these percentages being defined by weight relative to the total weight of the consumer product. Of course the above concentrations may be adapted according to the benefit effect desired in each product.

The invention will now be further described by way of examples. It will be appreciated that the invention as claimed is not intended to be limited in any way by these examples.

Examples

Example 1

Preparation of microcapsules by the process of the invention

Microcapsules A were prepared as follows.

7 g limonene were emulsified in 80 g WPI (Whey protein, Davisco) 2wt% solution prepared in DI water, using an ultra turrax. Then, 10 g HMP (High methoxy pectin, Fluka) 2wt% were then added under stirring to form WPI/HMP complex particles, so that WPI/HMP = 8 (w/w).

Then, the pH was adjusted to 5.35 using dilute NaOH and lactic acid solutions.

The emulsion was then heated to 85°C for 1 hour to induce the aggregation of the protein and form a microcapsules slurry (see figure 1 and figure 2).

Example 2Preparation of comparative microcapsules

5 This example shows the importance of preparing the WPI-stabilized emulsion before preparing the WPI/HMP complex particles.

In this example, the WPI/HMP=8 complex particles were prepared before adding the oil and emulsifying. Then, 10 g of WPI 5% solution was mixed with 3.1 g of HMP 2% solution and the pH was adjusted to 5.1.

1 g limonene was then added and the emulsion was formed by shearing with the ultra turrax.

10 Finally, the emulsion was heated to 85°C for 1 hour. No membrane was formed around the oil droplets (see figure 3).

Example 3Preparation of comparative microcapsules

15

Comparative microcapsules X without pectin were prepared as follows:

15 g limonene were added to 50 g WPI 10% solution and sheared with the ultra-turrax for 1 minute at 24000 rpm. Then, a solution of 2.5 g CaCl₂ (Acros) in 10 g deionized water was added slowly under stirring. The pH was then adjusted to 5.48 with dilute lactic acid and NaOH solutions, before heating the emulsion in a water bath at 85°C for 30 minutes with an overhead mechanical stirrer.

20

Example 4Preparation of microcapsules by the process of the invention

25 WPI/HMP microcapsules were prepared at pH~5.4 with different WPI/HMP ratios.

Table 1: Microcapsule compositions

	REFERENCE		WPI/HMP 8/1		WPI/HMP 5/1		WPI/HMP 3/1	
	<i>Comparative X</i>		<i>Capsule A</i>		<i>Capsule B</i>		<i>Capsule C</i>	
	g solution	%	g solution	%	g solution	%	g solution	%
WPI 10%	50	6.5%	50	4.6%	50	3.9%	50	3.1%
limonene	15	19.4%	15	13.8%	15	11.8%	15	9.3%
CaCl₂ 96%	2.5	3.1%	2.5	2.2%	2.5	1.9%	2.5	1.5%
DI Water	10	0.0%	10	0.0%	10	0.0%	10	0.0%
HMP 2%	0	0.0%	31	0.6%	50	0.8%	83.3	1.0%
pH	5.48		5.54		5.4		5.35	

For each sample, the WPI aqueous solution was denatured by heating 5 minutes at 80°C. After cooling down, the limonene was sheared in the WPI solution for 1 minute at 24000 rpm (ultra turrax) and the CaCl₂ solution was added under stirring. Then, the HMP solution was added still under stirring before adjusting the pH at circa 5.4 with dilute NaOH and lactic acid solutions, and heating at 85°C for 30 minutes, while mechanically stirring using an overhead stirrer.

The microcapsules slurries obtained were allowed to cool down.

- One can note from SEM pictures that the surface of the microcapsule of the invention (A, B and C – see figures 4,5,6 respectively) is smoother than for comparative microcapsules X (figure 7) underlying the presence of pectin in the membrane.

Example 5

Preparation of microcapsules by the process of the invention

9 g of a perfume oil A (see table 2) were added to 30 g of WPI solution (non-denatured at 80°C) and sheared with an ultra-turrax to form an emulsion. Then, a solution of 1.8 g CaCl₂ in 6 g water was added slowly while stirring, followed by 19.4 g of HMP 2% solution. After 15 minutes stirring, the emulsion was heated in a water bath at 85°C for 1 hour, while stirring with an over-head stirrer. Microcapsules D were obtained.

Table 2: Perfume oil A composition

Raw material	wt%
Romascone ^{®a)}	20
Verdox ^{TMb)}	20
Lorysia ^{®c)}	20
3-(4-isopropylphenyl)-2-methylpropanal	20
Salicynile ^{®d)}	20

- a) Methyl 2,2-dimethyl-6-methylene-1-cyclohexanecarboxylate, origin: Firmenich SA, Geneva, Switzerland
- 5 b) 2-tert-butyl-1-cyclohexyl acetate, trademark from International Flavors & Fragrances, USA
- c) 4-(1,1-diméthyléthyl)-1-cyclohexyl acetate, origin: Firmenich SA, Geneva, Switzerland
- d) (2Z)-2-phenyl-2-hexenenitrile, origin: Firmenich SA, Geneva, Switzerland
- 10 As shown in figure 8, the microcapsules obtained have a smooth surface and are spherical. One may also observe that at the end of a TGA analysis - Temperature program: 30-50°C at 10°C/min, 120 minutes at 50°C (see figure 9), the dry residue stands slightly below the theoretical dry residue, and corresponds to a retention of 82% of the initially encapsulated perfume.

15

Example 6

Evaluation of the barrier properties of the WPI/HMP membranes

- 20 To compare the volatiles retention as a function of the WPI/HMP ratio, the microcapsules slurries obtained in example 3 were diluted 20 times before applying ca 200 mg of diluted suspension on glass slides (dilution was performed to avoid HMP film-formation upon drying). The suspensions were allowed to dry onto the slides for 3 days. Afterwards, the dry residue was scratched with a spatula and the perfume released in the headspace was measured under a glass
- 25 bell using a photoionization detector (Tiger).

The amounts of limonene released from the dry microcapsules are represented on figure 10. The data were normalized by the amount of limonene theoretically deposited on each glass slide. According to the figure 10, one can conclude that reinforcing the WPI microcapsules with HMP (high methoxy pectin) improves the barrier properties.

5

Example 7

Performance in a flavored product (snack applications)

A- Chicken flavor

10

Microcapsules containing a chicken flavor were prepared using the same process as disclosed in example 1 with a ratio WPI/HMP=8 (~13.7wt% oil in the microcapsules suspension).

For comparison, an oil-in-water emulsion made of 7.9 g chicken flavor and 50 g gum Arabic 5wt% solution was prepared using an ultra-turrax (13.6wt% oil in the emulsion).

15 Then, 15 g of emulsion (for the Reference) or 15 g microcapsules suspension were coated onto 50 g of unflavored corn flakes using a rotating tumbler by spraying the suspension onto the corn flakes while rotating and drying by application of heat.

The obtained flavored corn flakes were then tasted by a group of 6 untrained panelists.

20 A strong flavor intensity was perceived with the corn flakes coated with the microcapsules.

To measure the flavor release, chewing was mimicked in wet conditions and the volatiles released were measured by a photoionization detector.

25 Procedure:

1 g flavored corn flakes were transferred in a 30-ml glass bottle with 1 g deionized water.

The mixture was allowed to equilibrate for 15 minutes. Volatiles measurement in the headspace was measured for 30 seconds, then the measurement was pursued while kneading the wet corn flakes with a spatula for 1 minute.

30 One can observe that more flavor is released from the cornflakes coated with microcapsules, before as well as after the kneading.

B- Lemon flavor

The same experiment was made with a lemon flavor instead of chicken flavor.

17 g of emulsion (for the Reference) or 17 g microcapsules suspension were coated onto 50 g of unflavored corn flakes using a rotating tumbler by spraying the suspension onto the corn flakes while rotating and drying by application of heat.

Chewing was mimicked by mixing 1 g corn flakes and 1 g deionized water. The volatiles released in the headspace were then measured by the photoionization detector before and after kneading as described above:

10

As for the chicken flavor, we observe a higher flavor release from the corn flakes coated with the microcapsules. This shows that microencapsulation enabled better volatiles retention during the coating process.

15

Example 8**Preparation of microcapsules cross-linked with glutaraldehyde**

15g limonene were sheared in 50 g of WPI 10wt% solution using an ultra turrax. Then a solution containing 3 g CaCl_2 in 10 g DI water was added while stirring, followed by 31 g of HMP 2% solution.

The pH was adjusted to 5.29.

The emulsion was heated 1 hour at 85°C while mechanically stirring. After cooling down, 0.10 g of glutaraldehyde 50% solution (Sigma) was added and the suspension was stirred 3 hours more at room temperature → microcapsules F are obtained

25

TGA was performed at 50°C on microcapsules F (sample diluted 5 times before TGA analysis). One can conclude from figure 11 that microcapsules F are stable according to TGA as shown by the curve lying above the dotted line (representing the theoretical dry content)

30

Example 9Microcapsules prepared by the process of the invention cross-linked with a polyisocyanate

Different amounts of diisocyanate (Takenate® D110-N - Trimethylol propane-adduct of xylylene diisocyanate, origin: Mitsui Chemicals, Inc., Japan – 2.3% and 3.3% of trimethylol propane-adduct of xylylene diisocyanate) were added in 9 g perfume oil A (see table 2) before emulsification in 30 g of a 10wt% WPI (whey protein isolate) solution, using the ultraturrax at 24000 rpm for 1 minute.

1.8 g of CaCl_2 dissolved in 6 g of deionized water were then added under magnetic stirring and the emulsion was allowed to stir for 10 minutes.

Then, 18.6 g of 2wt% high methoxy pectin (HMP) solution were added to the emulsion under stirring, before adjusting the pH to ~8.6 (8.5-9) with dilute NaOH solution.

The obtained emulsion was then heated with an overhead mechanical stirrer in a water bath at 70°C for 1 hour to induce the interfacial polymerisation.

After this first heating step, the pH was adjusted to 5.4 with dilute lactic acid and the slurry was heated at 85°C for 1 hour more to induce the denaturation of the protein. Microcapsules G (2.3% of Takenate®) and H (3.3% of Takenate®) were obtained.

Thermogravimetric analysis was performed at 50°C for 2 hours to evaluate the membrane barrier properties (TGA program: temperature ramp from 30 to 50°C at a rate of 10°C/minute, followed by a 2 hour-isotherm at 50°C).

All the samples were diluted 5-fold in deionized water before performing the analysis:

The dotted line represents the dry residue that should be remaining in the crucible at the end of the analysis if the microcapsules retain 100% perfume.

One can conclude from figure 12 that both capsules G and H are stable.

Evaluation of the stability of the microcapsules in a shower gel base:

A sufficient amount of microcapsule slurries G and H was weighed and mixed in the shower gel (Table 3) to add the equivalent of 0.2% perfume. The thus-obtained slurries were stored in closed vials at 38°C and perfume leakage was measured after recorded periods of time by GC-MS.

Table 3: Composition of the shower gel

Ingredients	Amount (% wt)
Deionised water	49.35
EDETA B Powder ¹⁾	0.05
Carbopol® Aqua SF-1 polymer ²⁾	6.00
Zetesol AO 328 U ³⁾	35.00
Sodium hydroxide 20% aqueous solution	1.00
Tego® Betain F 50 ⁴⁾	8.00
Kathon CG	0.10
Citric acid 40% aqueous solution	0.50

1) Tetrasodium EDTA; origin : BASF

2) Acrylates copolymer; origin: Noveon

5 3) Sodium C12-C15 Pareth Sulfate; origin: Zschimmer & Schwarz

4) Methylchloroisothiazolinone and methylisothiazolinone; origin: Rohm & Haas

One can conclude from figure 13 that, after 1 month storage at 38°C in the shower gel base, the microcapsules lost less than 3% of their perfume payload (see figure 13).

10

Example 10

Microcapsules prepared by the process of the invention cross-linked with a polyisocyanate

15 Microcapsules I were prepared as follows.

An oil phase containing 0.0966 g Takenate dissolved in 4.6195g of perfume oil B (see Table 4) was added into 15 g of a 10% WPI solution and sheared with an ultraturrax to form an O/W emulsion.

5 Table 4: Perfume oil B composition

Raw mat	% in oil
Ethyl 2-methyl-pentanoate	3.20%
Eucalyptol	7.80%
2,4-Dimethyl-3-cyclohexene-1-carbaldehyde ¹⁾	0.75%
Aldehyde C10	0.75%
Citronellyl Nitrile	4.30%
Isobornyl acetate	3.00%
Verdox ^{® 2)}	9.80%
Citronellyl Acetate	1.30%
2-Methylundecanal	3.00%
Diphenyloxide	0.80%
Aldehyde C12	1.30%
Dicyclopentadiene acetate	9.85%
Ionone beta	3.30%
Undecalactone gamma	18.75%
Hexyl Salicylate	15.90%
Benzyl Salicylate	16.20%
TOTAL	100%

1) Origin: Firmenich SA,
Switzerland

2) 2-tert-butyl-1-cyclohexyl acetate, origin and trademark from
IFF, USA

Then, 0.92 g CaCl₂ dissolved in 2.5 g deionized water was added dropwise to the emulsion while stirring, followed by slow addition of 9.55 g HMP 2% solution (final pH of the obtained emulsion is 5.37).

10 A first cross-linking step was performed by stirring the emulsion at room temperature for 4 hours, to form an internal shell by interfacial polymerization.

In a second step, the protein layer was heat-aggregated by heating the slurry at 85°C for 1 hour in a water bath.

In a last step, the external shell was cross-linked by glutaraldehyde as follows: the pH of the slurry was increased to pH 7.46 with dilute NaOH solution. Then 0.0874 g of a 50%

5 glutaraldehyde solution was added and the slurry was allowed to stir for 1 night.

TGA analysis of the sample performed at 50°C for 2 hours shows that the microcapsules obtained are thermally stable (see figure 14).

The stability of the microcapsules was also evaluated in a 5% SDS (sodium dodecyl sulfate) solution.

A few drops of the microcapsule slurry were added into 10 ml of SDS 5% solution and the microcapsules were observed through the microscope over time:

After 10 days in the SDS solution, the microcapsules remained spherical and release their oil upon pressure on the glass slide, which shows that they retained at least part of the encapsulated oil.

Example 11

Personal care compositions comprising the microcapsules of the invention

20 Microcapsules I are introduced in different body care applications as follows:

10 g of suspension was centrifuged for 5 minutes to recover a concentrate microcapsules cake.

The, 1 g of the concentrated microcapsules were incorporated in 10 g of 3 different unperfumed bases:

- Base 1: Deodorant stick without alcohol
- 25 - Base 2: Anti-perspirant stick with Al-Zr,
- Base 3: Day cream

The formulas of the bases are given below.

Table 5: Base 1 composition: Deodorant stick without alcohol

Ingredient	Amount (wt %)
Stearic acid (Part A)	5.05
1,2-propylene glycol (Part A)	41.87
Sodium hydroxide 20% aqueous solution (Part A)	4.24
Water (Part A)	30.30
Tetrasodium EDTA ¹⁾ (Part A)	0.10
Cetareth-25 ²⁾ (Part A)	1.52
PPG-3 Myristyl ether ³⁾ (Part A)	1.52
1,2-propylene glycol (Part B)	15.14
Triclosan ⁴⁾ (Part B)	0.25

1) Edeta[®] B Power; trademark and origin : BASF

2) Cremophor[®] A25; trademark and origin: BASF

5 3) Tegoso[®] APM; trademark and origin: Evonik

4) Irgasan[®] DP 300; trademark and origin : BASF

All the components of Part A are weighted (Table 5) and heated up to 70-75°C. Cetareth-25 is added once the other Part A ingredients are mixed and heated. Once the Cetareth-25 is dissolved, the Stearic Acid is added. Part B is prepared by dissolving the Triclosan in 1,2
 10 Propylene Glycol. Water which has evaporated is added. Slowly under mixing, Part B is poured into part A. To stock, a plastic bag into the bucket is put in to be sealed after cooling. Moulds was filled at about 70°C.

15 Table 6: Base 2 composition (Anti-perspirant stick with Al-Zr)

Ingredient	Amount (wt %)
Cyclomethicone ¹⁾ (Part A)	55.56
Stearyl Alcohol ²⁾ (Part A)	21.21

PPG-14 Butyl ether ³⁾ (Part A)	2.02
Hydrogenated Castor Oil ⁴⁾ (Part A)	1.01
Aluminium Zirconium tetrachlorohydrex-Gly ⁵⁾ (Part B)	20.20

- 1) Dow Corning[®] 345 Fluid; trademark and origin: Dow Corning
- 2) Lanette[®] 18; trademark and origin: BASF
- 3) Tegoso[®] PBE; trademark and origin: Evonik
- 4) Cutina[®] HR; trademark and origin: BASF
- 5) Summit AZP-908; trademark and origin: Reheis

All the components of Part A are weighted (Table 6), heated up to 70-75°C and mixed well. Ingredient of Part B is dispersed in Part A. The mixture is mixed and putted into a tick at 65 °C.

10 Table 7: Base 3 composition (Day cream)

Ingredients	%
ARLATONE 985 Ethoxylated Fatty Alcohol Ester	5.000
CETYL ALCOHOL	0.500
TEFOSE 2561 Ceteth-20 (and) Glyceryl Stearate (and) PEG-6 Stearate (and) Steareth-20	4.000
COSBIOL Squalan	1.000
MINERAL OIL 30-40 cp Paraffin Oil	2.000
PETROLEUM JELLY Petrolatum	6.000
WATER deionized	75.850

PROPYLENE GLYCOL	5.000
GLYDANT PLUS DMDM Hydantoin (and) Iodopropynyl Butylcarbamate	0.150
PNC 400 Sodium Carbomer	0.200
PERFUME	0.300
Total	100.00

Example 12

Performance of microcapsules in a fabric softener

5

Preparation of microcapsules J, K and L (cross-linked with a polyisocyanate)

Different amounts of diisocyanate (Takenate® D110-N - Trimethylol propane-adduct of xylylene diisocyanate, origin: Mitsui Chemicals, Inc., Japan) were added in 30 g of perfume oil B (see Table 4) before emulsification in 50 g of a 10wt% WPI (whey protein isolate) solution, using the ultraturrax at 24000 rpm for 1 minute.

3 g of CaCl₂ dissolved in 6 g of deionized water were then added under magnetic stirring and the emulsion was allowed to stir for 10 minutes.

Then, ca 31 g of 2wt% high methoxy pectin (HMP) solution were added to the emulsion under stirring. The pH was kept at the natural value of the mixture, which is between 5 and 5.5.

The obtained emulsion was then stirred with an overhead mechanical stirrer at room temperature for 4 hours to induce the interfacial polymerisation.

After this first step, the slurry was heated at 85°C for 1 hour to induce the denaturation of the protein.

Microcapsules J (2% of Takenate®), K (3% of Takenate®) and L (4% of Takenate®) were obtained.

20

Thermogravimetric analysis

Thermogravimetric analysis was performed at 50°C for 4 hours to evaluate the membrane barrier properties (TGA program: temperature ramp from 30 to 50°C at a rate of 10°C/minute, followed by a 4 hour-isotherm at 50°C). Results are displayed on figure 15.

5

The dotted line represents the dry residue that should be remaining in the crucible at the end of the analysis if the microcapsules retain 100% perfume.

One can conclude from figure 15 that capsules J and L are stable.

10 Perfume leakage

A sufficient amount of capsules L was weighed and mixed in the softener base (see composition in table 8) to add the equivalent of 0.116% perfume. The slurry was stored in closed vials at 38°C and perfume leakage was measured after recorded periods of time by GC-MS.

15 Table 8: Fabric softener composition

Ingredients	Amount (% wt)	Function
Methyl bis[ethyl(tallowate)] - 2- hydroxyethyl ammonium methyl sulfate ¹⁾	12.2	Softening agent
Calcium chloride sol 10%	0.4	Viscosity modifier
1,2-benzisothiazolin-3-one ²⁾	0.04	Preservative
Water	87.36	

1) Stepanex[®] VL 90A- Stepan

2) Proxel[®] GXL - Arch

20 The softener is prepared by weighting Methyl bis[ethyl (tallowate)]-2- hydroxyethyl ammonium methyl sulfate which was heated at 65°C. Then, Water and 1,2-benzisothiazolin-3-one are placed in the reactor and are heated at 65°C under stirring. To the above mixture is added Methyl bis[ethyl (tallowate)]-2- hydroxyethyl ammonium methyl sulfate. The mixture is stirred 15 minutes and CaCl₂ is added. Then microcapsules are added. The mixture is stirred 15 minutes

and is cooled down to room temperature under stirring (viscosity measured : result 35 +/- 5 mPas. (shear rate 106 sec⁻¹)).

One can conclude from the results of Figure 16 that the microcapsules are stable in a fabric softener at 38°C after 2 months.

Evaluation of the performance of microcapsules in softener application:

Deposition and performance of microcapsules was evaluated on cotton towels according to the following washing protocol:

10 Washing machine program: 40°C - short spinning - 900rpm

Towels: 24

The towels were then dried as follows:

Line drying (24hrs) – ambient temperature and humidity. One set of towels per panelist.

15 Panelists were asked to blindly evaluate the perfume intensity of towels before and after rubbing on a linear scale between 1 (=no odour) and 7 (very strong odour).

The evaluation was performed on the freshly prepared microcapsule slurry/softener base mixtures, as well as on the mixtures stored 1 month at 37°C (see table 9).

20 Table 9: Olfactive performance

	FRESH		After 1 month storage at 37°C	
	Before rubbing	After rubbing	Before rubbing	After rubbing
Capsules A	2.9	4.27	2.3	3.33
Capsules B	2.81	4.16	2.53	3.45
Capsules C	2.55	4.02	2.41	3.66

The rubbing effect was also measured, and is defined by the difference between the intensities before and after rubbing (δ) – see table 10.

Table 10: Olfactive performance

	Capsules F	Capsules G	Capsules H
δ (fresh)	1.37	1.36	1.47
δ (1 month at 37°C)	1.03	0.92	1.25

One can conclude that microcapsules of the present invention provide an olfactive boost after rubbing.

5

Example 13

Spray-dried microcapsules preparation

Emulsions A-E having the following ingredients are prepared.

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Table 11: Composition of Emulsions A-E and composition of granulated powder A-E after spray-drying

Ingredients	Emulsion A	Emulsion B	Emulsion C	Emulsion D	Emulsion E
Modified starch ¹⁾	2.6%	2.6%	2.6%	12.5%	2%
Maltodextrin ²⁾	26.8%	22.8%	19.3%	0%	19.1%
Maltose ³⁾	0%	0%	0%	7.9%	0%
Citric Acid	0%	0%	0%	1%	0%
Tripotassium Citrate	0%	0%	0%	1.9%	0%
Microcapsules I-L	12.0%	24%	37.0%	8.9%	56.2%
Silica ⁴⁾	1.1%	1.1%	1.1%	0%	0%
Free Perfume C ⁵⁾	0%	0%	0%	11%	0%

Water	57.6%	49.6%	40.1%	56.9%	22.7%
	Granule A	Granule B	Granule C	Granule D	Granule E
Modified starch ¹⁾	7.5%	7.4%	7.2%	31.6%	4.9%
Maltodextrin ²⁾	77.4%	65.5%	53.8%	0%	44.7%
Maltose	0%	0%	0%	20.9%	
Citric Acid	0%	0%	0%	2.6%	0%
Tripotassium citrate	0%	0%	0%	4.9%	0%
Encapsulated perfume C	0%	0%	0%	28.1%	0%
Microcapsules I-L	12.%	24.1%	36.1%	9.8%	48.4%
Silica	3.0	3.0%	2.9%	2.0%	2%
Fragrance loading in powder after spray-drying	10.1%	20.1%	30%	35.8%	40.2%

1) Capsul™, Ingredion

2) Maltodextrin 10DE origin: Roquette

3) Maltose, Lehmann & Voss

5 4) Silica, Evonik

5) see table 12

Table 12: Composition of Perfume C

Component	%
ACÉTATE DE 4-(1,1-DIMÉTHYLÉTHYL)-1-CYCLOHEXYLE ¹⁾	14.50
LINALOL BJ	10.50

LILIAL® ²⁾	10.00
ISO E SUPER ³⁾	10.00
CITRONELLYL NITRILE	9.00
DIPHENYLOXYDE	6.50
ISOBORNYL ACETATE	6.00
BETA IONONE	6.00
TRICYCLO[5.2.1.0~2,6~]DEC-3-EN-8-YL ACETATE (A) + TRICYCLO[5.2.1.0~2,6~]DEC-4-EN-8-YL ACETATE (B) 4)	5.50
ETHER MT	4.00
HEDIONE® ⁵⁾	4.00
GERANIOL 60	3.00
CITRAL	2.50
ALDEHYDE C 10	2.50
ALLYL HEPTANOATE	2.50
ETHYL METHYL-2-BUTYRATE	1.50
GERANYL ACETATE	1.00
2,4-DIMETHYL-3-CYCLOHEXENE-1-CARBALDEHYDE ⁶⁾	1.00

1) Firmenich SA, Switzerland

2) 3-(4-tert-butylphenyl)-2-methylpropanal, Givaudan SA, Vernier, Switzerland

3) 1-(octahydro-2,3,8,8-tetramethyl-2-naphthalenyl)-1-ethanone, International Flavors & Fragrances,

5 USA

4) Firmenich SA, Switzerland

5) Methyl dihydrojasmonate, Firmenich SA, Switzerland

6) Firmenich SA, Switzerland

10 Components for the polymeric matrix (Maltodextrin and capsulTM, or capsulTM, citric acid and tripotassium citrate) are added in water at 45-50°C until complete dissolution.

For emulsion D, free perfume C is added to the aqueous phase.

Microcapsules slurry is added to the obtained mixture. Then, the resulting mixture is then mixed gently at 25°C (room temperature).

Granulated powder A-E are prepared by spray-drying Emulsion A-E using a Sodeva Spray Dryer (Origin France), with an air inlet temperature set to 215°C and a throughput set to 500 ml per hour. The air outlet temperature is of 105°C. The emulsion before atomization is at ambient temperature.

Example 14

Liquid scent booster composition

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A sufficient amount of microcapsule slurry G, H, I, J, K or L is weighed and mixed in a liquid scent booster (Table 13) to add the equivalent of 0.2% perfume.

Table 13: Liquid scent booster composition

Ingredients	Amount (% wt)					
	1	2	3	4	5	6
Water	71.20%	89.5%	78.8%	79.4%	70%	70%
Propylene glycol	20.30%	-	-	-	20%	20%
Polyethylene glycol ethers of decyl alcohol ¹⁾	4.00%	6%				
Polyethylene glycol ether of Lauryl Alcohol ²⁾					4.00%	4.00%
alkyl polyglucoside C8-C10 ³⁾			8.30%	7.7%		
Deceth-3 ¹⁾	1.50%					
Lauryl lactate				1%		
Lauric acid		1.5%	1.60%			
Glyceryl Caprylate					3.00%	3.00%
Fragrance	3.00%	3.0%	3.00%	3.00%	3.00%	0%

15

1) Deceth-8; trademark and origin : KLK Oleo

- 2) Laureth-9; ; trademark and origin
- 3) Plantacare 2000UP; trademark and origin : BASF

5 Different ringing gel compositions are prepared (compositions 1-6) according to the following protocol.

In a first step, the aqueous phase (water), the solvent (propylene glycol) if present and surfactants are mixed together at room temperature under agitation with magnetic stirrer at 300 rpm for 5 min.

10 In a second step, the linker is dissolved in the hydrophobic active ingredient (fragrance) at room temperature under agitation with magnetic stirrer at 300 rpm. The resulting mixture is mixed for 5 min.

Then, the aqueous phase and the oil phase are mixed together at room temperature for 5 min leading to the formation of a transparent or opalescent ringing gel.

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Example 15

Liquid detergent composition

A sufficient amount of microcapsule slurry G, H, I, J, K or L is weighed and mixed in a liquid detergent (Table 14) to add the equivalent of 0.2% perfume.

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Table 14: Liquid detergent composition

Ingredients	Concentration [wt%]
Sodium C ₁₄₋₁₇ Alkyl Sec Sulfonate ¹⁾	7
Fatty acids, C ₁₂₋₁₈ and C ₁₈ -unsaturated ²⁾	7.5
C _{12/14} fatty alcohol polyglycol ether with 7 mol EO ³⁾	17
Triethanolamine	7.5
Propylene Glycol	11
Citric acid	6.5

Potassium Hydroxyde	9.5
Properase L ⁴⁾	0.2
Puradax EG L ⁴⁾	0.2
Purastar ST L ⁴⁾	0.2
Acrylates/Steareth-20 Methacrylate structuring Crosspolymer ⁵⁾	6
Deionized Water	27.4

1) Hostapur SAS 60; Origin: Clariant

2) Edenor K 12-18; Origin: Cognis

3) Genapol LA 070; Origin: Clariant

4) Origin: Genencor International

5) Aculyn 88; Origin: Dow Chemical

Example 16

Powder detergent composition

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A sufficient amount of granules A-E is weighed and mixed in a powder detergent composition (Table 15) to add the equivalent of 0.2% perfume.

Table 15: Powder detergent composition

15

Ingredients	Part
Anionic (Linear Alkyl Benzene Sulphonates)	20%
Nonionics (Alcohol Ethoxylates (5-9	6%

ethylene oxide)	
Builders (zeolites, sodium carbonate)	25%
Silicates	6%
Sodium Sulphate	35%
Others (Enzymes, Polymers, Bleach)	7.5%
Spray-dried granule powder A-E	0.5%

Example 17Concentrated All Purpose Cleaner composition

- 5 A sufficient amount of microcapsule slurry G, H, I, J, K or L is weighed and mixed in a concentrated all-purpose cleaner composition (Table 16) to add the equivalent of 0.2% perfume.

Table 16: concentrated all-purpose cleaner composition

Ingredients	Amount (% wt)	Function
Ethoxylated Alcohol (C9-C11, 8EO) ⁽¹⁾	20	Non-ionic surfactant
Sodium Dodecyl Benzene Sulfonate ⁽²⁾	16	Anionic surfactant
Sodium Cumene Sulfonate ⁽³⁾	8	Hydrotrope
Methyl chloro isothiazolinone Methyl isothiazolinone 3.3:1 ⁽⁴⁾	0.8%	preservative
Water	55.9	solvent

- 10 1) Neodol 91-8 ®; trademark and origin : Shell Chemical
 2) Biosoft D-40®; trademark and origin : Stepan Company
 3) Stepanate SCS®; trademark and origin : Stepan Company
 4) Kathon CG®; trademark and origin : Dow Chemical Company

All ingredients are mixed together and then the mixture was diluted with water to 100%.

Example 18Solid scent booster composition

The following compositions are prepared.

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Table 17: Salt-based solid scent booster compositions

Ingredients	Part
Sodium chloride	95
Spray-dried granule powder A-E	5

Table 18: Urea-based solid scent booster compositions

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Ingredients	Part
Urea (beads)	94
Spray-dried granule powder A-E	8
Bentonite	3
Perfume	3

Example 19Shampoo composition

- 15 A sufficient amount of microcapsule slurry G, H, I, J, K or L is weighed and mixed in a shampoo composition (Table 19) to add the equivalent of 0.2% perfume.

Table 19: Shampoo composition

	Ingredients	Concentration [wt%]
A	Water deionized	44.4
	Polyquaternium-10 ¹⁾	0.3
	Glycerin 85% ²⁾	1

	DMDM Hydantoin ³⁾	0.2
B	Sodium Laureth Sulfate ⁴⁾	28
	Cocamidopropyl Betaine ⁵⁾	3.2
	Disodium Cocoamphodiacetate ⁶⁾	4
	Ethoxy (20) Stearyl Alcohol ⁶⁾	1
C	Sodium Laureth Sulfate ⁴⁾	3
	Glyceryl Laureate ⁷⁾	0.2
D	Water deionized	1
	Sodium Methylparaben ⁸⁾	0.1
E	Sodium Chloride 10% aqueous sol.	15
	Citric acid 10% aqueous sol. till pH 5.5-6	q.s.
	Perfume	0.5
	T O T A L:	100

- 1) Ucare Polymer JR-400, Noveon
- 2) Schweizerhall
- 3) Glydant, Lonza
- 4) Texapon NSO IS, Cognis
- 5) Tego Betain F 50, Evonik
- 6) Amphotensid GB 2009, Zschimmer & Schwarz
- 7) Monomuls 90 L-12, Gruenau
- 8) Nipagin Monosodium, NIPA

Polyquaternium-10 is dispersed in water. The remaining ingredients of phase A are mixed separately by addition of one after the other while mixing well after each adjunction. Then this pre-mix is added to the Polyquaternium-10 dispersion and was mixed for 5 min. Then Phase B and the premixed Phase C (heat to melt Monomuls 90L-12 in Texapon NSO IS) are added. The

mixture is mixed well. Then, Phase D and Phase E are added while agitating. The pH was adjusted with citric acid solution till pH: 5.5 – 6.0.

Example 20

Shampoo composition

A sufficient amount of microcapsule slurry G, H, I, J, K or L is weighed and mixed in a shampoo composition (Table 20) to add the equivalent of 0.2% perfume.

Table 20: Shampoo composition

	Ingredients	Concentration [wt%]
A	Water deionized	45.97
	Tetrasodium EDTA ¹⁾	0.05
	Guar Hydroxypropyltrimonium Chloride ²⁾	0.05
	Polyquaternium-10 ³⁾	0.075
B	NaOH 10% aqueous sol.	0.3
C	Ammonium Lauryl Sulfate ⁴⁾	34
	Ammonium Laureth Sulfate ⁵⁾	9.25
	Cocamidopropyl Betaine ⁶⁾	2
	Dimethicone (&) C12-13 Pareth-4 (&) C12-13 Pareth-23 (&) Salicylic Acid ⁷⁾	2.5
D	Cetyl Alcohol ⁸⁾	1.2
	Cocamide MEA ⁹⁾	1.5
	Glycol Distearate ¹⁰⁾	2
E	Methylchloroisothiazolinone & Methylisothiazolinone ¹¹⁾	0.1

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	D-Panthenol 75% ¹²⁾	0.1
	Water deionized	0.3
F	Sodium Chloride 25% aqueous sol.	0.6
	T O T A L:	100

- 1) EDETA B Powder, BASF
- 2) Jaguar C14 S, Rhodia
- 3) Ucare Polymer JR-400, Noveon
- 4) Sulfetal LA B-E, Zschimmer & Schwarz
- 5) Zetesol LA, Zschimmer & Schwarz
- 6) Tego Betain F 50, Evonik
- 7) Xiameter MEM-1691, Dow Corning
- 8) Lanette 16, BASF
- 9) Comperlan 100, Cognis
- 10) Cutina AGS, Cognis
- 11) Kathon CG, Rohm & Haas
- 12) D-Panthenol, Roche

A premix comprising Guar Hydroxypropyltrimonium Chloride and Polyquaternium-10 are added to water and Tetrasodium EDTA while mixing. When the mixture is homogeneous, NaOH is added. Then, Phase C ingredients are added and the mixture was heat to 75 °C. Phase D ingredients are added and mixed till homogeneous. The heating is stopped and temperature of the mixture is decreased to RT. At 45 °C, ingredients of Phase E while mixing final viscosity is adjusted with 25% NaCl solution and pH of 5.5-6 is adjusted with 10% NaOH solution.

Example 21

Rinse-off hair composition

A sufficient amount of microcapsule slurry G, H, I, J, K or L is weighed and mixed in a rinse-off composition (Table 21) to add the equivalent of 0.2% perfume.

Table 21: rinse-off composition

	Ingredients	Concentration [wt%]
A	Water deionized	81.8
	Behentrimonium Chloride ¹⁾	2.5
	Hydroxyethylcellulose ²⁾	1.5
B	Cetearyl Alcohol ³⁾	4
	Glyceryl Stearate (and) PEG-100 Stearate ⁴⁾	2
	Behentrimonium Methosulfate (and) Cetyl alcohol (and) Butylene Glycol ⁵⁾	4
	Ethoxy (20) Stearyl Alcohol ⁶⁾	1
C	Amodimethicone (and) Trideceth-12 (and) Cetrimonium Chloride ⁷⁾	3
	Chlorhexidine Digluconate ⁸⁾ 20% aqueous solution	0.2
D	Citric acid 10% aqueous sol. till pH 3.5-4	q.s.
	T O T A L:	100

1) Genamin KDMP, Clariant

5 2) Tylose H10 Y G4, Shin Etsu

3) Lanette O, BASF

4) Arlacel 165, Croda

5) Incroquat Behenyl TMS-50-PA- (MH), Croda

6) Brij S20, Croda

10 7) Xiameter MEM-949, Dow Corning

8) Alfa Aesar

Ingredients of Phase A are mixed until an uniform mixture was obtained. Tylose is allowed to completely dissolve. Then the mixture is heated up to 70-75°C. Ingredients of Phase B are combined and melted at 70-75°C. Then ingredients of Phase B are added to Phase A with good

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agitation and the mixing is continued until cooled down to 60°C. Then, ingredients of Phase C are added while agitating and keeping mixing until the mixture cooled down to 40°C. The pH is adjusted with citric acid solution till pH: 3.5 – 4.0.

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Example 22**Antiperspirant spray anhydrous composition**

A sufficient amount of microcapsule slurry G, H, I, J, K or L is weighed and mixed in an antiperspirant spray anhydrous composition (Table 22) to add the equivalent of 0.2% perfume.

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Table 22: antiperspirant spray anhydrous composition

Ingredient	Amount (wt %)
Cyclomethicone ¹⁾	53.51
Isopropyl miristate	9.04
Silica ²⁾	1.03
Quaternium-18-Hectorite ³⁾	3.36
Aluminium Chlorohydrate ⁴⁾	33.06

1) Dow Corning[®] 345 Fluid; trademark and origin: Dow Corning

2) Aerosil[®] 200 ; trademark and origin : Evonik

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3) Bentone[®] 38; trademark and origin : Elementis Specialities

4) Micro Dry Ultrafine; origin : Reheis

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Using a high speed stirrer, Silica and Quaternium-18-Hectorite are added to the Isopropyl miristate and Cyclomethicone mixture. Once completely swollen, Aluminium Chlorohydrate is added portion wise under stirring until the mixture was homogeneous and without lumps. The aerosol cans are filled with 25 % Suspension of the suspension and 75 % of Propane/Butane (2,5 bar).

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Example 23Antiperspirant spray emulsion composition

A sufficient amount of microcapsule slurry G, H, I, J, K or L is weighed and mixed in
 5 antiperspirant spray emulsion composition (Table 23) to add the equivalent of 0.2% perfume.

Table 23: antiperspirant spray emulsion composition

Ingredient	Amount (wt %)
Polysorbate 65 ¹⁾ (Part A)	0.95
Polyglyceryl-2 dipolyhydroxystearate ²⁾ (Part A)	1.05
Cetyl PEG/PPG-10/1 Dimethicone ³⁾ (Part A)	2.75
Cyclomethicone ⁴⁾ (Part A)	16.4
Isopropylisostearate ⁵⁾ (Part A)	4.5
Phenoxyethanol ⁶⁾ (Part A)	0.5
Ethylhexylglycerin ⁷⁾ (Part A)	0.2
C12-15 Alkyl Benzoate ⁸⁾ (Part A)	5.65
Silica Silylate ⁹⁾ (Part A)	0.1
Sodium Methylparaben ¹⁰⁾ (Part B)	0.1
Aluminium Chlorohydrate ¹¹⁾ (Part B)	20
Water (Part B)	44.47
Fragrance (Part C)	3.33

- 10 1) Tween 65; trademark and origin : CRODA
 2) Dehymuls PGPH; trademark and origin : BASF
 3) Abil EM-90; trademark and origin : BASF
 4) Dow Corning 345 fluid; trademark and origin : Dow Corning
 5) Crodamol ipis; trademark and origin : CRODA

- 6) Phenoxyethanol; trademark and origin : LANXESS
 7) Sensiva sc 50; trademark and origin : KRAFT
 8) Tegosoft TN; trademark and origin : Evonik
 9) Aerosil R 812; trademark and origin : Evonik
 5 10) Nipagin mna; trademark and origin : CLARIANT
 11) Locron L; trademark and origin : CLARIANT

The ingredients of Part A and Part B are weighted separately. Ingredients of Part A are heated up to 60°C and ingredients of Part B are heated to 55 °C. Ingredients of Part B are poured small
 10 parts while continuous stirring into A. Mixture were stirred well until the room temperature was reached. Then, ingredients of part C are added. The emulsion is mixed and is introduced into the aerosol cans. The propellant is crimped and added.

Aerosol filling: 30% Emulsion: 70% Propane / Butane 2,5 bar
 15

Example 24

Deodorant spray composition

A sufficient amount of microcapsule slurry G, H, I, J, K or L is weighed and mixed in
 20 antiperspirant deodorant spray composition (Table 24) to add the equivalent of 0.2% perfume.

Table 24: deodorant spray composition

Ingredient	Amount (wt %)
Ethanol 95 %	90.65
Triclosan ¹⁾	0.26
Isopropyl miristate	9.09

1) Irgasan[®] DP 300; trademark and origin : BASF

25

All the ingredients according to the sequence of the Table 24 are mixed and dissolved. Then the aerosol cans are filled, crimp and the propellant is added (Aerosol filling: 40% active solution 60% Propane / Butane 2.5 bar).

Example 25Antiperspirant roll-on emulsion composition

A sufficient amount of microcapsule slurry G, H, I, J, K or L is weighed and mixed in
 5 antiperspirant roll-on emulsion composition (Table 25) to add the equivalent of 0.2% perfume.

Table 25: antiperspirant roll-on emulsion composition

Ingredient	Amount (wt %)
Steareth-2 ¹⁾ (Part A)	3.25
Steareth-21 ²⁾ (Part A)	0.75
PPG-15 Stearyl Ether ³⁾ (Part A)	4
WATER deionised (Part B)	51
Aluminum Chlorohydrate 50% aqueous solution ⁴⁾ (Part C)	40
Fragrance (Part D)	1

- 1) BRIJ 72; origin : ICI
 10 2) BRIJ 721; origin : ICI
 3) ARLAMOL E; origin : UNIQEMA-CRODA
 4) LOCRON L; origin : CLARIAN

Part A and B are heated separately to 75°C; Part A is added to part B under stirring and the
 15 mixture is homogenized for 10 minutes. Then, the mixture is cooled down under stirring; and
 part C is slowly added when the mixture reached 45°C and part D when the mixture reached at
 35 °C while stirring. Then the mixture is cooled down to RT.

Example 26Antiperspirant roll-on composition

20

A sufficient amount of microcapsule slurry G, H, I, J, K or L is weighed and mixed in
 antiperspirant roll-on composition (Table 26) to add the equivalent of 0.2% perfume.

Table 26: antiperspirant roll-on composition

Ingredient	QUANTITY
Water (Part A)	45
Aluminum Chlorohydrate 50% aqueous solution ¹⁾ (Part B)	20
Alcohol Denat. (Ethanol 96%) (Part B)	30
Ceteareth-12 ²⁾ (Part C)	2
Ceteareth-30 ³⁾ (Part C)	2
Fragrance (Part D)	1

1) LOCRON L; origin: CLARIANT

2) EUMULGIN B-1; origin : BASF

5 3) EUMULGIN B-3; origin : BASF

The ingredients of part B are mixed in the vessel then ingredient of part A is added. Then dissolved part C in part A and B. With perfume, 1 part of Cremophor RH40 for 1 part of perfume is added while mixing well

10

Example 27

Antiperspirant roll-on composition

A sufficient amount of microcapsule slurry G, H, I, J, K or L is weighed and mixed in

15 antiperspirant roll-on emulsion composition (Table 27) to add the equivalent of 0.2% perfume.

Table 27: antiperspirant roll-on emulsion composition

Ingredient	Amount (wt %)
Water (Part A)	50.51
Hydroxyethylcellulose ¹⁾ (Part A)	0.71
Ethanol 95 % (Part B)	40.40
1,2-Propylene Glycol (Part B)	5.05
Triclosan ²⁾ (Part B)	0.30

PEG-40 Hydrogenated castor oil ³⁾ (Part C)	3.03
---	------

- 1) Natrosol[®] 250 H; trademark and origin: Ashland
- 2) Irgasan[®] DP 300; trademark and origin : BASF
- 3) Cremophor[®] RH 40; trademark and origin : BASF

- 5 Part A is prepared by sprinkling little by little the Hydroxyethylcellulose in the water whilst rapidly stirring with the turbine. Stirring is continued until the Hydroxyethylcellulose is entirely swollen and giving a limpid gel. Then, Part B is poured little by little in Part A whilst continuing stirring until the whole is homogeneous. Part C is added.

10

Example 28Deodorant pump without alcohol formulation

A sufficient amount of microcapsule slurry G, H, I, J, K or L is weighed and mixed in the following composition (Table 28) to add the equivalent of 0.2% perfume.

15

Table 28: deodorant composition

Ingredients	Amount (wt %)
C12-15 Alkyl Lactate ¹⁾	5
Dimethicone ²⁾	91.6
Cetyl Lactate ³⁾	1
Octyldodecanol ⁴⁾	0.8
Triclosan ⁵⁾	0.1
PERFUME	1.5

- 1) Ceraphyl 41; trademark and origin ASHLAND
- 2) DOW CORNING 200 FLUID 0.65cs; trademark and origin DOW CORNING CORPORATION
- 3) Ceraphyl 28; trademark and origin ASHLAND
- 4) Eutanol G; trademark and origin BASF
- 5) Irgasan[®] DP 300; trademark and origin : BASF

20

All the ingredients of Table 28 are mixed according to the sequence of the table and the mixture is heated slightly to dissolve the Cetyl Lactate.

5

Example 29

Deodorant pump with alcohol formulation

A sufficient amount of microcapsule slurry G, H, I, J, K or L is weighed and mixed in the following composition (Table 29) to add the equivalent of 0.2% perfume.

10

Table 29: deodorant composition

Ingredients	Amount (wt %)
Ethyl Alcohol (Part A)	60
PEG-6 Caprylic/Capric Glycerides ¹⁾ (Part A)	2
Water (Part A)	35.6
PEG-40 Hydrogenated Castor Oil ²⁾ (Part B)	0.4
PERFUME (Part B)	2

1) Softigen 767; trademark and origin CRODA

2) Cremophor[®] RH 40; trademark and origin : BASF

15 Ingredients from Part B are mixed together. Ingredients of Part A are dissolved according to the sequence of the Table and are poured into part B.

Example 30

Talc formulation

20

A sufficient amount of granules A-E is weighed and mixed in introduced in a standard talc base: 100% talc, very slight characteristic odor, white powder, origin: LUZENAC to add the equivalent of 0.2% perfume.

Example 31Shower-gel Reference

- 5 A sufficient amount of microcapsule slurry G, H, I, J, K or L is weighed and mixed in the following composition (Table 30) to add the equivalent of 0.2% perfume.

Table 30: shower gel composition

Ingredients	Amount (% wt)	Function
WATER deionised	49.350	Solvent
Tetrasodium EDTA ¹⁾	0.050	Chelating agent
Acrylates Copolymer ²⁾	6.000	Thickener
Sodium C12-C15 Pareth Sulfate ³⁾	35.000	Surfactant
Sodium Hydroxide 20% aqueous solution	1.000	pH adjuster
Cocamidopropyl Betaine ⁴⁾	8.000	Surfactant
Methylchloroisothiazolinone and Methylisothiazolinone ⁵⁾	0.100	Preservative
Citric Acid (40%)	0.500	pH adjuster

10 3) EDETA B POWDER; trademark and origin: BASF

4) CARBOPOL AQUA SF-1 POLYMER; trademark and origin: NOVEON

5) ZETESOL AO 328 U; trademark and origin: ZSCHIMMER & SCHWARZ

6) TEGO-BETAIN F 50; trademark and origin: GOLDSCHMIDT

7) KATHON CG; trademark and origin: ROHM & HASS

15

Ingredients are mixed, pH is adjusted to 6-6.3 (Viscosity: 4500cPo +/-1500cPo (Brookfield RV / Spindle#4 / 20RPM)).

Example 32Shower-gel composition

20

A sufficient amount of microcapsule slurry G, H, I, J, K or L is weighed and mixed in the following composition (Table 31) to add the equivalent of 0.2% perfume.

Table 31: shower gel composition

Ingredients	Amount (% wt)	Function
WATER deionized	52.40	Solvent
Tetrasodium EDTA ¹⁾	0.10	Chelating agent
Sodium Benzoate	0.50	Preservative
Propylene Glycol	2.00	Solvent
Sodium C12-C15 Pareth Sulfate ²⁾	35.00	Surfactant
Cocamidopropyl Betaine ³⁾	8.00	Surfactant
Polyquaternium-7 ⁴⁾	0.20	Conditioning agent
Citric Acid (40%)	1.00	pH adjuster
Sodium Chloride	0.80	Viscosity adjuster

1) EDETA B POWDER; trademark and origin: BASF

2) ZETESOL AO 328 U; trademark and origin: ZSCHIMMER & SCHWARZ

5 3) TEGO-BETAIN F 50; trademark and origin: GOLDSCHMIDT

4) MERQUAT 550; trademark and origin: LUBRIZOL

Ingredients are mixed, pH is adjusted to 4.5 (Viscosity: 3000cPo +/-1500cPo (Brookfield RV / Spindle#4 / 20RPM)).

10

Example 33

Shower-gel composition

15 A sufficient amount of microcapsule slurry G, H, I, J, K or L is weighed and mixed in the following composition (Table 32) to add the equivalent of 0.2% perfume.

Table 32: shower gel composition

Ingredients	Amount (% wt)	Function
WATER deionized	50.950	Solvent
Tetrasodium EDTA ¹⁾	0.050	Chelating agent
Sodium Benzoate	0.500	Preservative

Glycerin 86%	3.500	Solvent
Sodium Laureth Sulfate ²⁾	27.000	Surfactant
Polyquaternium-7 ³⁾	1.000	Conditioning Agent
Coco-Betaine ⁴⁾	6.000	Surfactant
PEG-120 Methyl Glucose trioleate ⁵⁾	1.000	Thickener
Citric Acid (40%)	1.000	pH adjuster
Glycol Distearate & Laureth-4 & Cocamidopropyl Betaine ⁶⁾	3.000	Pearlizing agent
Sodium Chloride 20%	5.000	Viscosity adjuster
PEG-40 Hydrogenated Castor Oil ⁷⁾	1.000	Viscosity adjuster

1) EDETA B POWDER; trademark and origin: BASF

2) Texapon NSO IS; trademark and origin: COGNIS

3) MERQUAT 550; trademark and origin: LUBRIZOL

4) DEHYTON AB-30; trademark and origin: COGNIS

5) GLUCAMATE LT; trademark and origin: LUBRIZOL

6) EUPERLAN PK 3000 AM; trademark and origin: COGNIS

7) CREMOPHOR RH 40; trademark and origin: BASF

Ingredients are mixed, pH is adjusted to 4.5 (Viscosity: 4000cPo +/-1500cPo (Brookfield RV / Spindle#4 / 20RPM))

Example 34

Hand Dishwash

15

A sufficient amount of microcapsule slurry G, H, I, J, K or L is weighed and mixed in the following composition (Table 33) to add the equivalent of 0.2% perfume.

Table 33: Hand dishwash composition

20

Ingredients	Amount (% wt)	Function
Linear alkylbenzene sulfonic	20	Anionic surfactant

acid ⁽¹⁾		
Diethanolamide ⁽²⁾	3.5	Foam booster
Sodium Hydroxide (50%) ⁽³⁾	3.4	pH Adjuster/neutralizer
Secondary alcohol ethoxolate ⁽⁴⁾	2.5	Non-ionic surfactant
Sodium xylene sulfonate	6.3	Hydrotrope
Water	64.3	Solvent

1) Biosoft S-118®; trademark and origin : Stepan Company

2) Ninol 40-CO®; trademark and origin : Stepan Company

3) Stepanate SXS®; trademark and origin : Stepan Company

4) Tergitol 15-S-9®; trademark and origin : Dow Chemical Company

5

Water with sodium hydroxide and diethanolamide are mixed. LAS is added. After the LAS is neutralized, the remaining ingredients are added. The pH was Checked (=7-8) and adjusted if necessary.

10

Example 35

Toothpaste formulation

A sufficient amount of microcapsule slurry M (corresponding to microcapsules A except that a menthol flavor is encapsulated) is weighed and mixed in the following composition (Table 34) to add the equivalent of 0.2% flavor.

15

Table 34: Toothpaste formulation

Ingredients	Amount (% wt)
Polyethylene glycol 400	2.0%
Xanthan Gum	0.6%
Sorbitol 70% Solution	50%

73

Sodium Fluoride	0.220%
Sodium Benzoate	0.2%
Water	15.230%
Hydrated Silica ¹⁾	22.0%
Hydrated Silica ²⁾	7.0%
Titanium Dioxide CI77891	0.5%
Sodium Lauryl Sulfate	1.250%
Flavor	1.2%
TOTAL	100%

1) Tixosil 73; trademark and origin :

2) Tixosil 43; trademark and origin :

Example 36

5

Dicalcium Phosphate based toothpaste formulation

A sufficient amount of microcapsule slurry M (corresponding to microcapsules A except that a menthol flavor is encapsulated) is weighed and mixed in the following composition (Table 35) to add the equivalent of 0.2% flavor.

10 Table 35: Toothpaste formulation

Ingredients	Amount (% wt)
Sodium carboxymethyl cellulose	1.2%
Flavor	1.2%
DI/Purified Water	Q.S to Final Wt.
Sodium Lauryl Sulfate	1.3%
Glycerine	20.0%
Sodium Saccharin	0.2%
Dicalcium phosphate dihydrate	36.0%
Methylparaben	0.2%

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Silica ¹⁾	3.0%
TOTAL	100%

1) Aerosil®200; trademark and origin:

Example 37

Mouthwash alcohol free formulation

5

A sufficient amount of microcapsule slurry M (corresponding to microcapsules A except that a menthol flavor is encapsulated) is weighed and mixed in the following composition (Table 36) to add the equivalent of 0.2% flavor.

10 Table 36: Mouthwash formulation

Ingredients	Amount (% wt)
Propylene Glycol	10%
Flavor	0.240%
DI/Purified Water	Q.S to Final Wt.
Poloxamer 407 NF	0.240%
Sodium Lauryl Sulfate	0.040%
Sorbitol 70% Solution	10.0%
Sodium Saccharin	0.030%
Glycerine	3.0%
Sodium Benzoate	0.100%
Sucralose	0.020%
Benzoic Acid	0.050%
TOTAL	100%

Example 38Mouthwash formulation

A sufficient amount of microcapsule slurry M (corresponding to microcapsules A except that a menthol flavor is encapsulated) is weighed and mixed in the following composition (Table 37) to

5 add the equivalent of 0.2% flavor.

Table 37: Mouthwash formulation

Ingredients	Amount (% wt)
Ethyl Alcohol 190 Proof	15.0%
Flavor	0.240%
DI/Purified Water	Q.S to Final Wt.
Poloxamer 407 NF	0.240%
Sodium Lauryl Sulfate	0.040%
Sorbitol 70% Solution	10.0%
Sodium Saccharin	0.030%
Glycerine	3.0%
Sodium Benzoate	0.100%
Sucralose	0.020%
Benzoic Acid	0.050%
TOTAL	100%

CLAIMS

1- A process for preparing a core-shell microcapsules slurry, said process comprising the steps of:

- 5 a) dispersing an oil phase comprising a perfume, into an aqueous phase comprising a globular protein to form an oil-in-water emulsion;
- b) adding an aqueous solution comprising a polysaccharide into the oil-in-water emulsion; and
- 10 c) applying sufficient condition to induce the denaturation of the protein to form core-shell microcapsules in the form of a slurry,

characterized by the fact that the mean oil droplet size in the oil-in-water emulsion is greater than 10 microns, and wherein the microcapsules are not agglomerated, and characterized by the fact that:

- 15 - a polyfunctional monomer is further dissolved in the oil phase in step a), and
- the process comprises a further step before step c) consisting of applying conditions sufficient to induce interfacial polymerization of the polyfunctional monomer.

2- The process according to claim 1, characterized by the fact that the globular protein is chosen in the group consisting of whey protein, beta-lactoglobulin, ovalbumine, bovine serum albumin, vegetable protein, and mixtures thereof.

3- The process according to claim 1 or claim 2, characterized by the fact that the polysaccharide is chosen in the group consisting of pectin, carrageenans, alginate, and mixtures thereof.

4- The process according to any one of the preceding claims, characterized by the fact that the protein is whey protein and the polysaccharide is pectin, preferably high methoxy pectin.

- 5- The process according to any one of the preceding claims, characterized by the fact that the denaturation of the protein in step c) is induced by a heating step.
- 5 6- The process according to claim 5, characterized by the fact that the heating step is carried out at a temperature T_{den} comprised between 50 and 100°C, preferably between 80 and 100°C.
- 10 7- The process according to any one of the preceding claims, characterized by the fact that the weight ratio between the oil phase and the protein is comprised between 1 and 10.
- 8- The process according to any one of the preceding claims, characterized by the fact that the weight ratio between the protein and the polysaccharide is comprised between 1 and 10.
- 15 9- The process according to any one of the preceding claims, characterized by the fact that a calcium solution is further added in the emulsion obtained in step a) and/ or in the mixture obtained in step b).
- 20 10- The process according to any one of the preceding claims, characterized by the fact that a crosslinker, preferably chosen in the group consisting of transglutaminase, glutaraldehyde, genipin, and mixtures thereof is added in the mixture obtained in step b) and/or in the mixture obtained in step c).
- 25 11- A microcapsules slurry comprising at least one microcapsule made of:
- an oil-based core comprising a perfume,
 - an inner shell comprising a polyfunctional monomer,
 - an outer shell comprising a protein and a polysaccharide, wherein the protein is preferably whey protein and wherein the polysaccharide is preferably pectin,
- 30 wherein the microcapsules have a mean size greater than 10 microns, and wherein the microcapsules are not agglomerated.

12- The microcapsules slurry according to claim 11, wherein the microcapsules are made of:

- an oil-based core comprising a perfume,
- an inner shell made of a polymerized polyisocyanate having at least two isocyanate functional groups and an outer shell comprising whey protein and pectin.

5

13- A composition comprising microcapsules as defined in claim 11 or claim 12, wherein the composition is in the form of a perfumed product, preferably chosen in the group consisting of body care products, laundry care products.