PHOSPHOROUS BASED CORE-SHELL MICROCAPSULES

Field of the invention

The present invention relates to phosphorous based microcapsules. A process for the preparation of said microcapsules is also an object of the invention. Perfuming compositions and consumer products comprising said microcapsules, in particular perfumed consumer products in the form of home care or personal care products, are also part of the invention.

Background of the invention

One of the problems faced by the perfumery industry lies in the relatively rapid loss of olfactive benefit provided by odoriferous compounds due to their volatility, particularly that of “top-notes”. In order to tailor the release rates of volatiles, delivery systems such as microcapsules containing a perfume are needed to protect and later release the core payload when triggered. A key requirement from the industry regarding these systems is to survive suspension in challenging bases without physically dissociating or degrading. This is referred to as stability for the delivery system. For instance, fragranced personal and household cleansers containing high levels of aggressive surfactant detergents are very challenging for the stability of microcapsules.

Polyurea and polyurethane-based microcapsule slurry are widely used for example in perfumery industry for instance as they provide a long lasting pleasant olfactory effect after their applications on different substrates. Those microcapsules have been widely disclosed in the prior art.

In addition to the performance in terms of stability and olfactive performance, the consumer demand for eco-friendly delivery systems is more and more important and is driving the development of new delivery systems.

There is therefore still a need to provide new microcapsules using more eco-friendly materials, while not compromising on the performance of the microcapsules, in particular in terms of stability in a challenging medium such as a consumer product base, as well as in delivering a good performance in terms of active ingredient delivery, e.g. olfactive performance in the case of perfuming ingredients.

The present invention is proposing a solution to the above-mentioned problem by providing new phosphorous based microcapsules and a process for preparing said microcapsules.

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 "**microcapsule**", or the similar, in the present invention it is meant that core-shell microcapsules have a particle size distribution in the micron range (e.g. a mean diameter (d(v, 0.5)) comprised preferably between about 1 and 3000 microns, more preferably between 1 and 500 microns) and comprise an external solid polymeric shell and an internal continuous oil phase enclosed by the external shell.

By "**phosphorous-based microcapsule**", it should be understood that the shell comprises a phosphorous compound, in particular a phosphate compound.

In an embodiment, the shell is an inorganic/organic hybrid-based shell.

By "**microcapsule slurry**", it is meant microcapsule(s) that is (are) dispersed in a liquid. In an embodiment, the slurry is an aqueous slurry, i.e the microcapsule(s) is (are) dispersed in an aqueous phase.

"**Dispersing phase**" and "**continuous phase**" can be used indifferently in the present invention.

By "**polyfunctional monomer**", it is meant a molecule that, as unit, reacts or binds chemically to form a polymer or a supramolecular polymer. The polyfunctional monomer of the invention has at least two functional groups that are capable to react with or bind to functional groups of another component and/or are capable to polymerize to form a polymeric shell.

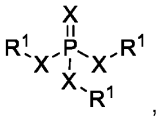
CORE-SHELL MICROCAPSULES

The present invention relates to a core-shell microcapsule comprising:

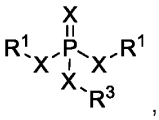
- a core comprising a hydrophobic material, preferably comprising a perfume oil, and

- a shell obtainable from a polymerization reaction of at least one phosphorous compound of formula (I) and/or one compound of formula (II), and/or one compound of formula (III),

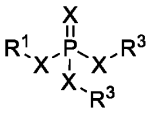
wherein the compound of formula (I) to (III) are as following:



Formula (I)



Formula (II)



Formula (III)

wherein

X, each independently, represents O, S, and/or N-R^2,

R^1, each independently, represents R^4-Y_n with n representing an integer from 1 to 6,

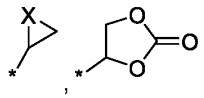
R^2, each independently, represent H or a C_1 to C_{10} hydrocarbon moiety, optionally comprising one or more O, S and/or N atoms,

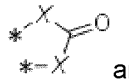
R^3, each independently, represent a H, Na^+, K^+, or a C_1 to C_{10} hydrocarbon moiety, optionally comprising one or more O, S and/or N atoms,

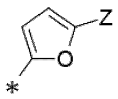
R^4, each independently, represents a C_1 to C_{20} hydrocarbon moiety, optionally comprising one or more O, S and/or N atoms, and

Y, each independently, represents

- -OH, -SH, -NHR^2, -CHO, -NCO and/or -COCl;
- a strained heterocycle of the following structures:

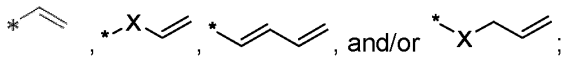


, a 5- or 6- membered ring comprising  and/or



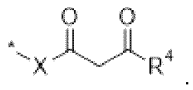
wherein Z is H or –CHO;

- a free-radical polymerizable function like (meth)acrylates and/or (meth)acrylamides and/or maleimide;
- one of the following olefins:



and/or

- one of the following malonate functions:



Hydrophobic material

According to the invention, the core-shell microcapsule comprises a core comprising a hydrophobic material.

According to an embodiment, the core is an oil-based core.

The hydrophobic material according to the invention can be “inert” material like solvents or active ingredients.

By “hydrophobic material”, it is meant any hydrophobic material which forms a two-phase dispersion when mixed with water. The hydrophobic material is typically liquid at about 20°C.

According to an embodiment, the hydrophobic material is a hydrophobic active ingredient.

When the hydrophobic materials is an active ingredient, it is preferably chosen from the group consisting of flavor(s), flavor ingredient(s), perfume(s), perfume ingredient(s), nutraceutical(s), cosmetic(s), agrochemical ingredient(s), pest control agent(s), biocide active(s) and mixtures thereof.

According to a particular embodiment, the hydrophobic material comprises a phase change material (PCM).

According to a particular embodiment, the hydrophobic material comprises a mixture of a perfume with another ingredient selected from the group consisting of nutraceuticals, cosmetics, pest control agents, agrochemical ingredients and biocide actives.

According to a particular embodiment, the hydrophobic material comprises a mixture of biocide actives with another ingredient selected from the group consisting of perfumes, nutraceuticals, cosmetics, pest control agents.

According to a particular embodiment, the hydrophobic material comprises a mixture of pest control agents with another ingredient selected from the group consisting of perfumes, nutraceuticals, cosmetics, biocide actives.

According to a particular embodiment, the hydrophobic material comprises a perfume.

According to a particular embodiment, the hydrophobic material consists of a perfume.

According to a particular embodiment, the hydrophobic material consists of biocide actives.

According to a particular embodiment, the hydrophobic material consists of pest control agents.

According to a particular embodiment, the hydrophobic material comprises, preferably consists, of phytosanitary compounds.

According to a particular embodiment, the hydrophobic material comprises preferably consists of crop fertilizers.

The term “phytosanitary compound” refers to substances, formulations, or compositions designed to protect plants from pests, diseases, or other harmful organisms. These compounds include, but are not limited to, fungicides, insecticides, herbicides, nematicides, bactericides, acaricides, molluscicides, growth regulators, biopesticides, and other plant-protecting agents. Phytosanitary compounds may be of synthetic or natural origin and can function by inhibiting the growth or activity of target organisms, repelling pests, or enhancing plant resistance to biotic and abiotic stress factors.

The term “crop fertilizer” refers to any substance or composition that is applied to soil, plants, or other growing media to supply essential nutrients, enhance soil fertility, or promote plant growth and development. Crop fertilizers include, but are not limited to, macronutrient and micronutrient formulations, organic and inorganic fertilizers, controlled-release fertilizers, biofertilizers, composts, manure-based fertilizers, and soil amendments. These fertilizers may be in solid, or liquid form and can be applied through various methods, including foliar application, soil incorporation, fertigation, and hydroponic solutions.

By “perfume” (or also “perfume oil”) what is meant here is an ingredient or a composition that is a liquid at about 20°C. According to any one of the above embodiments said perfume oil can be a perfuming ingredient alone or a mixture of ingredients in the form of a perfuming composition. As a “perfuming ingredient” it is meant here a compound, which is used for the primary purpose of conferring or modulating an odor. 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. For the purpose of the present invention, perfume oil also includes a combination of perfuming ingredients with substances which together improve, enhance or modify the delivery of the perfuming ingredients, such as perfume precursors, modulators, emulsions or dispersions, as well as combinations which impart an additional benefit beyond that of modifying or imparting an odor, such as long-lastingness, blooming, malodor counteraction, antimicrobial effect, microbial stability, pest control.

The nature and type of the perfuming 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 sulfurous heterocyclic compounds and essential oils (for example Thyme oil), 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 perfumery.

In particular one may cite perfuming ingredients which are commonly used in perfume formulations, such as:

- Aldehydic ingredients: decanal, dodecanal, 2-methyl-undecanal, 10-undecenal, octanal, nonanal and/or nonenal;
- Aromatic-herbal ingredients: eucalyptus oil, camphor, eucalyptol, 5-methyltricyclo[6.2.1.$0^{2,7}$]undecan-4-one, 1-methoxy-3-hexanethiol, 2-ethyl-4,4-dimethyl-1,3-oxathiane, 2,2,7/8,9/10-tetramethylspiro[5.5]undec-8-en-1-one, menthol and/or alpha-pinene;
- Balsamic ingredients: coumarin, ethylvanillin and/or vanillin;
- Citrus ingredients: dihydromyrcenol, citral, orange oil, linalyl acetate, citronellyl nitrile, orange terpenes, limonene, 1-p-menthen-8-yl acetate and/or 1,4(8)-p-menthadiene;
- Floral ingredients: methyl dihydrojasmonate, linalool, citronellol, phenylethanol, 3-(4-tert-butylphenyl)-2-methylpropanal, hexylcinnamic aldehyde, benzyl acetate, benzyl salicylate, tetrahydro-2-isobutyl-4-methyl-4(2H)-pyranol, beta ionone, methyl 2-(methylamino)benzoate, (E)-3-methyl-4-(2,6,6-trimethyl-2-cyclohexen-1-yl)-3-buten-2-one, (1E)-1-(2,6,6-trimethyl-2-cyclohexen-1-yl)-1-penten-3-one, 1-(2,6,6-trimethyl-1,3-cyclohexadien-1-yl)-2-buten-1-one, (2E)-1-(2,6,6-trimethyl-2-cyclohexen-1-yl)-2-buten-1-one, (2E)-1-[2,6,6-trimethyl-3-cyclohexen-1-yl]-2-buten-1-one, (2E)-1-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2-buten-1-one, 3-(3,3/1,1-dimethyl-5-indanyl)propanal, 2,5-dimethyl-2-indanmethanol, 2,6,6-trimethyl-3-cyclohexene-1-carboxylate, 3-(4,4-dimethyl-1-cyclohexen-1-yl)propanal, hexyl salicylate, 3,7-dimethyl-1,6-nonadien-3-ol, 3-(4-isopropylphenyl)-2-methylpropanal, verdyl acetate, geraniol, p-menth-1-en-8-ol, 4-(1,1-dimethylethyl)-1-cyclohexyle acetate, 1,1-dimethyl-2-phenylethyl acetate, 4-cyclohexyl-2-methyl-2-butanol, amyl salicylate , high cis methyl dihydrojasmonate, 3-methyl-5-phenyl-1-pentanol, verdyl proprionate, geranyl acetate, tetrahydro linalool, cis-7-p-menthanol, propyl (S)-2-(1,1-dimethylpropoxy)propanoate, 2-methoxynaphthalene, 2,2,2-trichloro-1-phenylethyl acetate, 4/3-(4-hydroxy-4-methylpentyl)-3-cyclohexene-1-carbaldehyde, amylcinnamic aldehyde, 8-decen-5-olide, 4-phenyl-2-butanone, isononyle acetate, 4-(1,1-dimethylethyl)-1-cyclohexyl acetate, verdyl isobutyrate and/or mixture of methylionones isomers;
- Fruity ingredients: gamma-undecalactone, 2,2,5-trimethyl-5-pentylcyclopentanone, 2-methyl-4-propyl-1,3-oxathiane, 4-decanolide, ethyl 2-methyl-pentanoate, hexyl acetate, ethyl 2-methylbutanoate, gamma-nonalactone, allyl heptanoate, 2-

phenoxyethyl isobutyrate, ethyl 2-methyl-1,3-dioxolane-2-acetate, diethyl 1,4-cyclohexanedicarboxylate, 3-methyl-2-hexen-1-yl acetate, 1-[3,3-dimethylcyclohexyl]ethyl [3-ethyl-2-oxiranyl]acetate and/or diethyl 1,4-cyclohexane dicarboxylate;

- Green ingredients: 2-methyl-3-hexanone (E)-oxime, 2,4-dimethyl-3-cyclohexene-1-carbaldehyde, 2-tert-butyl-1-cyclohexyl acetate, styrallyl acetate, allyl (2-methylbutoxy)acetate, 4-methyl-3-decen-5-ol, diphenyl ether, (Z)-3-hexen-1-ol and/or 1-(5,5-dimethyl-1-cyclohexen-1-yl)-4-penten-1-one;
- Musk ingredients: 1,4-dioxa-5,17-cycloheptadecanedione, (Z)-4-cyclopentadecen-1-one, 3-methylcyclopentadecanone, 1-oxa-12-cyclohexadecen-2-one, 1-oxa-13-cyclohexadecen-2-one, (9Z)-9-cycloheptadecen-1-one, 2-{(1S)-1-[(1R)-3,3-dimethylcyclohexyl]ethoxy}-2-oxoethyl propionate, 3-methyl-5-cyclopentadecen-1-one, 4,6,6,7,8,8-hexamethyl-1,3,4,6,7,8-hexahydrocyclopenta[g]isochromene, (1S,1'R)-2-[1-(3',3'-dimethyl-1'-cyclohexyl)ethoxy]-2-methylpropyl propanoate, oxacyclohexadecan-2-one and/or (1S,1'R)-[1-(3',3'-dimethyl-1'-cyclohexyl)ethoxycarbonyl]methyl propanoate;
- Woody ingredients: 1-[(1RS,6SR)-2,2,6-trimethylcyclohexyl]-3-hexanol, 3,3-dimethyl-5-[(1R)-2,2,3-trimethyl-3-cyclopenten-1-yl]-4-penten-2-ol, 3,4'-dimethylspiro[oxirane-2,9'-tricyclo[6.2.1.$0^{2,7}$]undec[4]ene, (1-ethoxyethoxy)cyclododecane, 2,2,9,11-tetramethylspiro[5.5]undec-8-en-1-yl acetate, 1-(octahydro-2,3,8,8-tetramethyl-2-naphtalenyl)-1-ethanone, patchouli oil, terpenes fractions of patchouli oil, Clearwood®, (1'R,E)-2-ethyl-4-(2',2',3'-trimethyl-3'-cyclopenten-1'-yl)-2-buten-1-ol, 2-ethyl-4-(2,2,3-trimethyl-3-cyclopenten-1-yl)-2-buten-1-ol, methyl cedryl ketone, 5-(2,2,3-trimethyl-3-cyclopentenyl)-3-methylpentan-2-ol, 1-(2,3,8,8-tetramethyl-1,2,3,4,6,7,8,8a-octahydronaphthalen-2-yl)ethan-1-one and/or isobornyl acetate;
- Other ingredients (e.g. amber, powdery spicy or watery): dodecahydro-3a,6,6,9a-tetramethyl-naphtho[2,1-b]furan and any of its stereoisomers, heliotropin, anisic aldehyde, eugenol, cinnamic aldehyde, clove oil, 3-(1,3-benzodioxol-5-yl)-2-methylpropanal, 7-methyl-2H-1,5-benzodioxepin-3(4H)-one, 2,5,5-trimethyl-1,2,3,4,4a,5,6,7-octahydro-2-naphthalenol, 1-phenylvinyl acetate, 6-methyl-7-oxa-1-thia-4-azaspiro[4.4]nonane and/or 3-(3-isopropyl-1-phenyl)butanal.

It is also understood that said ingredients may also be compounds known to release in a controlled manner various types of perfuming compounds also known as properfume or profragrance. Non-limiting examples of suitable properfumes may include 4-(dodecylthio)-4-(2,6,6-trimethyl-2-cyclohexen-1-yl)-2-butanone, 4-(dodecylthio)-4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2-butanone, 3-(dodecylthio)-1-(2,6,6-trimethyl-3-cyclohexen-1-yl)-1-butanone, 2-(dodecylthio)octan-4-one, 2-phenylethyl oxo(phenyl)acetate, 3,7-dimethylocta-

2,6-dien-1-yl oxo(phenyl)acetate, (Z)-hex-3-en-1-yl oxo(phenyl)acetate, 3,7-dimethyl-2,6-octadien-1-yl hexadecanoate, bis(3,7-dimethylocta-2,6-dien-1-yl) succinate, (2-((2-methylundec-1-en-1-yl)oxy)ethyl)benzene, 1-methoxy-4-(3-methyl-4-phenethoxybut-3-en-1-yl)benzene, (3-methyl-4-phenethoxybut-3-en-1-yl)benzene, 1-(((Z)-hex-3-en-1-yl)oxy)-2-methylundec-1-ene, (2-((2-methylundec-1-en-1-yl)oxy)ethoxy)benzene, 2-methyl-1-(octan-3-yloxy)undec-1-ene, 1-methoxy-4-(1-phenethoxyprop-1-en-2-yl)benzene, 1-methyl-4-(1-phenethoxyprop-1-en-2-yl)benzene, 2-(1-phenethoxyprop-1-en-2-yl)naphthalene, (2-phenethoxyvinyl)benzene, 2-(1-((3,7-dimethyloct-6-en-1-yl)oxy)prop-1-en-2-yl)naphthalene, (2-((2-pentylcyclopentylidene)methoxy)ethyl)benzene, 4-allyl-2-methoxy-1-((2-methoxy-2-phenylvinyl)oxy)benzene, (2-((2-heptylcyclopentylidene)methoxy)ethyl)benzene, 1-isopropyl-4-methyl-2-((2-pentylcyclopentylidene)methoxy)benzene, 2-methoxy-1-((2-pentylcyclopentylidene)methoxy)-4-propylbenzene, 3-methoxy-4-((2-methoxy-2-phenylvinyl)oxy)benzaldehyde, 4-((2-(hexyloxy)-2-phenylvinyl)oxy)-3-methoxybenzaldehyde or a mixture thereof.

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, triethyl 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 C_1 to C_4 alkyl or alkenyl substituent;
- Group 2: perfuming ingredients comprising a cyclopentane, cyclopentene, cyclopentanone or cyclopentenone ring substituted with at least one linear or branched C_4 to C_8 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 C_5 to C_8 alkyl or alkenyl substituent or with at least one phenyl substituent and optionally one or more linear or branched C_1 to C_3 alkyl or alkenyl substituents;
- Group 4: perfuming ingredients comprising at least two fused or linked C_5 and/or C_6 rings;

- Group 5: perfuming ingredients comprising a camphor-like ring structure;
- Group 6: perfuming ingredients comprising at least one C_7 to C_{20} 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 substitutent;

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, 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, (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, tetrahydro-4-methyl-2-phenyl-2H-pyran (origin: Firmenich SA, Geneva, Switzerland), cyclohexyl acetate, cyclanol acetate, 1,4-cyclohexane diethyldicarboxylate (origin: Firmenich SA, Geneva, Switzerland), (3RS,3aRS,6SR,7ASR)-perhydro-3,6-dimethyl-benzo[B]furan-2-one (origin: Firmenich SA, Geneva, Switzerland), ((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;
- 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), (1'R,E)-3,3-dimethyl-5-(2',2',3'-trimethyl-3'-cyclopenten-1'-yl)-4-penten-2-ol (origin: Firmenich SA, Geneva, Switzerland), 2-heptylcyclopentanone, methyl-cis-3-oxo-2-pentyl-1-cyclopentane acetate (origin: Firmenich SA, Geneva, Switzerland), 2,2,5-trimethyl-5-pentyl-1-cyclopentanone (origin: Firmenich SA, Geneva, Switzerland), 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);
- Group 3: damascones, 1-(5,5-dimethyl-1-cyclohexen-1-yl)-4-penten-1-one (origin: Firmenich SA, Geneva, Switzerland), (1'R)-2-[2-(4'-methyl-3'-cyclohexen-1'-yl)propyl]cyclopentanone, alpha-ionone, beta-ionone, damascenone, 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), 1-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2-buten-1-one (origin: Firmenich SA, Geneva, Switzerland), (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), 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, Geneva, Switzerland), (E)-3-methyl-4-(2,6,6-trimethyl-2-cyclohexen-1-yl)-3-buten-2-one, terpenyl isobutyrate, 4-(1,1-dimethylethyl)-1-cyclohexyl acetate (origin: Firmenich SA, Geneva, Switzerland), 8-methoxy-1-p-menthene, (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;

- Group 4: Methyl cedryl ketone (origin: International Flavors and Fragrances, USA), a mixture of (1RS,2SR,6RS,7RS,8SR)-tricyclo[5.2.1.$0^{2,6}$]dec-3-en-8-yl 2-methylpropanoate and (1RS,2SR,6RS,7RS,8SR)-tricyclo[5.2.1.$0^{2,6}$]dec-4-en-8-yl 2-methylpropanoate, vetyverol, vetyverone, 1-(octahydro-2,3,8,8-tetramethyl-2-naphtalenyl)-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), a mixture of 3-(3,3-dimethyl-5-indanyl)propanal and 3-(1,1-dimethyl-5-indanyl)propanal (origin: Firmenich SA, Geneva, Switzerland), 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, (perhydro-5,5,8A-trimethyl-2-naphthalenyl acetate (origin: Firmenich SA, Geneva, Switzerland), octalynol, (dodecahydro-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;
- Group 5: camphor, borneol, isobornyl acetate, 8-isopropyl-6-methyl-bicyclo[2.2.2]oct-5-ene-2-carbaldehyde, pinene, camphene, 8-methoxycedrane, (8-methoxy-2,6,6,8-tetramethyl-tricyclo[5.3.1.0(1,5)]undecane (origin: Firmenich SA, Geneva, Switzerland), cedrene, cedrenol, cedrol, 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, Switzerland), 3-methoxy-7,7-dimethyl-10-methylene-bicyclo[4.3.1]decane (origin: Firmenich SA, Geneva, Switzerland);
- Group 6: (trimethyl-13-oxabicyclo-[10.1.0]-trideca-4,8-diene (origin: Firmenich SA, Geneva, Switzerland), 9-hexadecen-16-olide (origin: Firmenich SA, Geneva, Switzerland), pentadecenolide (origin: Firmenich SA, Geneva, Switzerland), 3-methyl-(4/5)-

cyclopentadecenone ,(origin: Firmenich SA, Geneva, Switzerland), 3-methylcyclopentadecanone (origin: Firmenich SA, Geneva, Switzerland), pentadecanolide (origin: Firmenich SA, Geneva, Switzerland), cyclopentadecanone (origin: Firmenich SA, Geneva, Switzerland), 1-ethoxyethoxy)cyclododecane (origin: Firmenich SA, Geneva, Switzerland), 1,4-dioxacycloheptadecane-5,17-dione, 4,8-cyclododecadien-1-one;

- Group 7: (+-)-2-methyl-3-[4-(2-methyl-2-propanyl)phenyl]propanal (origin: Givaudan SA, Vernier, Switzerland), 2,2,2-trichloro-1-phenylethyl acetate.

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.

According to a particular embodiment, 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/cm^3.

"*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 odor 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/cm^3 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/cm^3 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 group consisting of (+-)-1-methoxy-3-hexanethiol, 4-(4-hydroxy-1-phenyl)-2-butanone, 2-methoxy-4-(1-propenyl)-1-phenyl acetate, pyrazobutyle, 3-propylphenol, 1-(3-methyl-1-benzofuran-2-yl)ethanone, 2-(3-phenylpropyl)pyridine, 1-(3,3/5,5-dimethyl-1-cyclohexen-1-yl)-4-penten-1-one , 1-(5,5-dimethyl-1-cyclohexen-1-yl)-4-penten-1-one, a mixture comprising (3RS,3aRS,6SR,7ASR)-perhydro-3,6-dimethyl-benzo[b]furan-2-one and (3SR,3aRS,6SR,7ASR)-perhydro-3,6-dimethyl-benzo[b]furan-2-one, (+-)-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, H-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, mixture comprising (+-)-5,6-dihydro-4-methyl-2-phenyl-2H-pyran and tetrahydro-4-methylene-2-phenyl-2H-pyran, mixture comprising 4-methylene-2-phenyltetrahydro-2H-pyran and (+-)-4-methyl-2-phenyl-3,6-dihydro-2H-pyran, 4-hydroxy-3-methoxybenzaldehyde, nonylenic aldehyde, 2-methoxy-4-propylphenol, 3-methyl-5-phenyl-2-pentenenitrile, 1-(spiro[4.5]dec-6/7-en-7-yl)-4-penten-1-one(, 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 damascone ((2E)-1-[(1RS,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-aminobenzoate, ethyl

methylphenylglycidate, octalactone gamma, 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, beta ionone, (+-)-6-pentyltetrahydro-2H-pyran-2-one, (3E,5Z)-1,3,5-undecatriene, 10-undecenal, (9E)-9-undecenal (9Z)-9-undecenal, (Z)-4-decenal, (+-)-ethyl 2-methylpentanoate, 1,2-diallyldisulfane, 2-tridecenenitrile, 3-tridecenenitrile, , (+-)-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, (+-)-5E3-methyl-5-cyclopentadecen-1-one, cyclopropylmethyl 3-hexenoate, (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-(3-oxo-2-pentylcyclopentyl)acetate, 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, (4E)-3,3-dimethyl-5-[(1R)-2,2,3-trimethyl-3-cyclopenten-1-yl]-4-penten-2-ol, 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, (1R,4R,5R)-4,7,7-trimethyl-6-thiabicyclo[3.2.1]octane, (-)-(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 (2/3-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, and mixtures thereof.

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.

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.

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-based core may have therefore a Log T>-4.

According to an embodiment, the perfume raw materials having a Log T>-4 are chosen in the group consisting of ethyl 2-methylbutyrate, (E)-3-phenyl-2-propenyl acetate, (+-)-6/8-sec-butylquinoline, (+-)-3-(1,3-benzodioxol-5-yl)-2-methylpropanal, verdyl 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, dodecanal, 1-oxa-12/13-cyclohexadecen-2-one, (+-)-3-(4-isopropylphenyl)-2-methylpropanal, aldehyde C11, (+-)-2,6-dimethyl-7-octen-2-ol, allyl 3-cyclohexylpropanoate, (Z)-3-hexenyl acetate, 5-methyl-2-(2-propanyl)cyclohexanone, allyl heptanoate, 2-(2-methyl-2-propanyl)cyclohexyl acetate, 1,1-dimethyl-2-phenylethyl butyrate, geranyl acetate, neryl acetate, (+-)-1-phenylethyl acetate, 1,1-dimethyl-2-phenylethyl acetate, 3-methyl-2-butenyl acetate, ethyl 3-oxobutanoate, (2Z)-ethyl 3-hydroxy-2-butenoate, 8-p-menthanol, 8-p-menthanyl acetate, 1-p-menthanyl acetate, (+-)-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, 2,4,6-trimethyl-3-cyclohexene-1-carbaldehyde, 2-cyclohexylethyl acetate, octanal, ethyl butanoate, (+-)-(3E)-4-(2,6,6-trimethyl-1/2-cyclohexen-1-yl)-3-buten-2-one, 1-[(1RS,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, decanal, 2-phenylethyl acetate, (1S,2S,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol, (1S,2R,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol), (+-)-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, (3S)-1-[(1R,6S)-2,2,6-trimethylcyclohexyl]-3-hexanol, (3R)-1-[(1S,6S)-2,2,6-trimethylcyclohexyl]-3-hexanol, (+)-(1S,1'R)-2-[1-(3',3'-dimethyl-1'-cyclohexyl)ethoxy]-2-methylpropyl propanoate, and mixtures thereof.

According to an embodiment, the core comprises a perfume formulation comprising:

- 0 to 60 wt.% of a hydrophobic solvent (based on the total weight of the perfume formulation),
- 40 to 100 wt.% of a perfume oil (based on the total weight of the perfume formulation), wherein the perfume oil has at least two, preferably all of the following characteristics:
    - at least 35%, preferably at least 40%, preferably at least 50%, more preferably at least 60% of perfuming ingredients having a log P above 3, preferably above 3.5,

- at least 20%, preferably at least 25%, preferably at least 30%, more preferably at least 40% of Bulky materials of groups 1 to 6, preferably 3 to 6 as herein defined and
- at least 15%, preferably at least 20%, more preferably at least 25%, even more preferably at least 30% of high impact perfume materials having a Log T < -4,

optionally, further hydrophobic active ingredients.

According to a particular embodiment, the perfume comprises 0 to 60 wt.% of a hydrophobic solvent.

According to a particular embodiment, the hydrophobic solvent is a density balancing material preferably chosen in the group consisting of benzyl salicylate, benzyl benzoate, cyclohexyl salicylate, benzyl phenylacetate, phenylethyl phenylacetate, triacetin, ethyl citrate, methyl and ethyl salicylate, benzyl cinnamate, and mixtures thereof.

In an embodiment, the hydrophobic solvent has Hansen Solubility Parameters compatible with entrapped perfume oil.

The term "Hansen solubility parameter" is understood refers to a solubility parameter approach proposed by Charles Hansen used to predict polymer solubility and was developed around the basis that the total energy of vaporization of a liquid consists of several individual parts. To calculate the "weighted Hansen solubility parameter" one must combine the effects of (atomic) dispersion forces, (molecular) permanent dipole-permanent dipole forces, and (molecular) hydrogen bonding (electron exchange). The weighted Hansen solubility parameter" is calculated as $(\delta D^2 + \delta P^2 + \delta H^2)^{0.5}$, wherein δD is the Hansen dispersion value (also referred to in the following as the atomic dispersion fore), δP is the Hansen polarizability value (also referred to in the following as the dipole moment), and δH is the Hansen Hydrogen-bonding ("h-bonding") value (also referred to in the following as hydrogen bonding). For a more detailed description of the parameters and values, see Charles Hansen, The Three Dimensional Solubility Parameter and Solvent Diffusion Coefficient, Danish Technical Press (Copenhagen, 1967).

Euclidean difference in solubility parameter between a fragrance and a solvent is calculated as $(4*(\delta D_{solvent}-\delta D_{fragrance})^2 + (\delta P_{solvent}-\delta P_{fragrance})^2 + (\delta H_{solvent}-\delta H_{fragrance})^2)^{0.5}$, in which $\delta D_{solvent}$, $\delta P_{solvent}$, and $\delta H_{solvent}$, are the Hansen dispersion value, Hansen polarizability value, and Hansen h-bonding values of the solvent, respectively; and $\delta D_{fragrance}$, $\delta P_{fragrance}$, and $\delta H_{fragrance}$ are the Hansen dispersion value, Hansen polarizability value, and Hansen h-bonding values of the fragrance, respectively.

In an embodiment, the perfume oil and the hydrophobic solvent have at least two Hansen solubility parameters selected from a first group consisting of: an atomic dispersion

force (δD) from 12 to 20, a dipole moment (δP) from 1 to 8, and a hydrogen bonding (δH) from 2.5 to 11.

In an embodiment, the perfume oil and the hydrophobic solvent have at least two Hansen solubility parameters selected from a second group consisting of: an atomic dispersion force (δD) from 12 to 20, preferably from 14 to 20, a dipole moment (δP) from 1 to 8, preferably from 1 to 7, and a hydrogen bonding (δH) from 2.5 to 11, preferably from 4 to 11.

In an embodiment, at least 90% of the perfume oil, preferably at least 95% of the perfume oil, most preferably at least of 98% of the perfume oil has at least two Hansen solubility parameters selected from a first group consisting of: an atomic dispersion force (δD) from 12 to 20, a dipole moment (δP) from 1 to 8, and a hydrogen bonding (δH) from 2.5 to 11.

In an embodiment, the perfume oil and the hydrophobic solvent have at least two Hansen solubility parameters selected from a second group consisting of: an atomic dispersion force (δD) from 12 to 20, preferably from 14 to 20, a dipole moment (δP) from 1 to 8, preferably from 1 to 7, and a hydrogen bonding (δH) from 2.5 to 11, preferably from 4 to 11.

According to an embodiment, the perfuming formulation comprises a fragrance modulator (that can be used in addition to the hydrophobic solvent when present or as substitution of the hydrophobic solvent when there is no hydrophobic solvent).

Preferably, the fragrance modulator is defined as a fragrance material with

i. a vapor pressure of less than 0.0008 Torr at 22°C;
ii. a clogP of 3.5 and higher, preferable 4.0 and higher and more preferable 4.5
iii. at least two Hansen solubility parameters selected from a first group consisting of: an atomic dispersion force from 12 to 20, a dipole moment from 1 to 7, and a hydrogen bonding from 2.5 to 11,
iv. at least two Hansen solubility parameters selected from a second group consisting of: an atomic dispersion force from 14 to 20, a dipole moment from 1 to 8, and a hydrogen bonding from 4 to 11, when in solution with a compound having a vapor pressure range of 0.0008 to 0.08 Torr at 22°C.

Preferably, as examples the following ingredients can be listed as modulators but the list in not limited to the following materials: alcohol C12, oxacyclohexadec-12/13-en-2-one, 3-[(2',2',3'-trimethyl-3'-cyclopenten-1'-yl)methoxy]-2-butanol, cyclohexadecanone, (Z)-4-cyclopentadecen-1-one, cyclopentadecanone, (8Z)-oxacycloheptadec-8-en-2-one, 2-[5-(tetrahydro-5-methyl-5-vinyl-2-furyl)-tetrahydro-5-methyl-2-furyl]-2-propanol, muguet aldehyde, 1,5,8-trimethyl-13-oxabicyclo[10.1.0]trideca-4,8-diene, (+-)-4,6,6,7,8,8-hexamethyl-1,3,4,6,7,8-hexahydrocyclopenta[g]isochromene, (+)-(1S,2S,3S,5R)-2,6,6-trimethylspiro[bicyclo[3.1.1]heptane-3,1'-cyclohexane]-2'-en-4'-one, oxacyclohexadecan-2-one, 2-{(1S)-1-[(1R)-3,3-dimethylcyclohexyl]ethoxy}-2-oxoethyl propionate, (+)-(4R,4aS,6R)-4,4a-dimethyl-6-(1-propen-2-yl)-4,4a,5,6,7,8-hexahydro-2(3H)-naphthalenone, amylcinnamic

aldehyde, hexylcinnamic aldehyde, hexyl salicylate, (1E)-1-(2,6,6-trimethyl-1-cyclohexen-1-yl)-1,6-heptadien-3-one, (9Z)-9-cycloheptadecen-1-one.

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 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 .

The term "biocide" refers to a chemical substance capable of killing living organisms (e.g. microorganisms) or reducing or preventing their growth and/or accumulation. Biocides are commonly used in medicine, agriculture, forestry, and in industry where they prevent the fouling of, for example, water, agricultural products including seed, and oil pipelines. A biocide can be a pesticide, including a fungicide, herbicide, insecticide, algicide, molluscicide, miticide and rodenticide; and/or an antimicrobial such as a germicide, antibiotic, antibacterial, antiviral, antifungal, antiprotozoal and/or antiparasite.

As used herein, a "pest control agent" indicates a substance that serves to repel or attract pests, to decrease, inhibit or promote their growth, development or their activity. Pests refer to any living organism, whether animal, plant or fungus, which is invasive or troublesome to plants or animals, pests include insects notably arthropods, mites, spiders, fungi, weeds, bacteria and other microorganisms.

By "flavor oil", it is meant here a flavoring ingredient or a mixture of flavoring ingredients, solvents or adjuvants of current use for the preparation of a flavoring 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 flavor and/or taste. Flavoring ingredients are well known to a person skilled in the art and their nature does not warrant a detailed description here, which in any case would not be exhaustive, the skilled flavorist 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 flavoring 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, van Nostrand Co., Inc. Solvents and adjuvants of current use for the preparation of a flavoring formulation are also well known in the art.

In an embodiment, the flavor is a mint flavor. In a more particular embodiment, the mint is selected from the group consisting of peppermint and spearmint.

In a further embodiment, the flavor is a cooling agent or mixtures thereof.

In another embodiment, the flavor is a menthol flavor.

Flavors that are derived from or based on fruits where citric acid is the predominant, naturally-occurring acid include but are not limited to, for example, citrus fruits (e.g. lemon, lime), limonene, strawberry, orange, and pineapple. In one embodiment, the flavors food is lemon, lime or orange juice extracted directly from the fruit. Further embodiments of the flavor comprise the juice or liquid extracted from oranges, lemons, grapefruits, key limes, citrons, clementines, mandarins, tangerines, and any other citrus fruit, or variation or hybrid thereof. In an embodiment, the flavor comprises a liquid extracted or distilled from oranges, lemons, grapefruits, key limes, citrons, clementines, mandarins, tangerines, any other citrus fruit or variation or hybrid thereof, pomegranates, kiwifruits, watermelons, apples, bananas, blueberries, melons, ginger, bell peppers, cucumbers, passion fruits, mangos, pears, tomatoes, and strawberries.

In an embodiment, the flavor comprises a composition that comprises limonene, In an embodiment, the composition is a citrus that further comprises limonene.

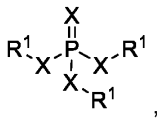
In another particular embodiment, the flavor comprises a flavor selected from the group comprising strawberry, orange, lime, tropical, berry mix, and pineapple.

The phrase flavor includes not only flavors that impart or modify the smell of foods but include taste imparting or modifying ingredients. The latter do not necessarily have a taste or smell themselves but are capable of modifying the taste that other ingredients provides, for instance, salt enhancing ingredients, sweetness enhancing ingredients, umami enhancing ingredients, bitterness blocking ingredients and so on.

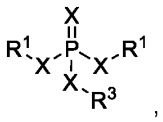
In a further embodiment, suitable sweetening components may be included in the particles described herein. In an embodiment, a sweetening component is selected from the group consisting of sugar (e.g., but not limited to sucrose), a stevia component (such as but not limited to stevioside or rebaudioside A), sodium cyclamate, aspartame, sucralose, sodium saccharine, and Acesulfam K or mixtures thereof.

Phosphorous compound

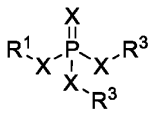
According to the invention, the core-shell microcapsule comprises a shell obtainable from a polymerization reaction of at least one phosphorous compound of formula (I) and/or one compound of formula (II), and/or one compound of formula (III), wherein the phosphorous compound of formula (I) to (III) are as following:



Formula (I)



Formula (II)



Formula (III)

wherein

X, each independently, represents O, S, and/or N-R^2,

R^1, each independently, represents R^4-Y_n with n representing an integer from 1 to 6,

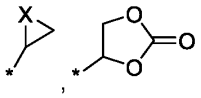
R^2, each independently, represents H or a C_1 to C_{10} hydrocarbon moiety, optionally comprising one or more O, S and/or N atoms,

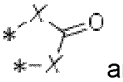
R^3, each independently, represents a C_1 to C_{10} hydrocarbon moiety, optionally comprising one or more O, S and/or N atoms,

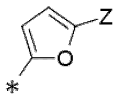
R^4, each independently, represents a H, Na^+, K^+ or a C_1 to C_{20} hydrocarbon moiety, optionally comprising one or more O, S and/or N atoms, and

Y, each independently, represents

- -OH, -SH, -NHR^2, -CHO, -NCO, and/or -COCl;
- a strained heterocycle of the following structures:

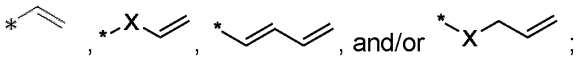


, a 5- or 6- membered ring comprising  and/or



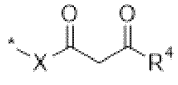
wherein Z is H or –CHO;

- a free-radical polymerizable function like (meth)acrylates and/or (meth)acrylamides and/or maleimide;
- one of the following olefins:



and/or

- one of the following malonate functions:



.

The terms “alkyl” and “alkenyl” are understood as comprising branched, alicyclic and linear alkyl and alkenyl groups. The terms “alkenyl”, “cycloalkenyl” and “heterocycloalkenyl” are understood as comprising 1, 2 or 3 olefinic double bonds, preferably 1 or 2 olefinic double

bonds, provided that the cycloalkenyl group is not an aryl group. The terms “cycloalkyl”, “cycloalkenyl”, “heterocycloalkyl” and “heterocycloalkenyl” are understood as comprising a monocyclic or fused, spiro and/or bridged bicyclic or tricyclic cycloalkyl, cycloalkenyl, heterocycloalkyl and heterocycloalkenyl groups, preferably monocyclic cycloalkyl, cycloalkenyl, heterocycloalkyl and heterocycloalkenyl groups. The term “alkoxy” is understood as an -OR’ group wherein R’ is a linear branched or cyclic alkyl group. The term “C1-4 carboxylic ester group” is understood as -OC(=O)R’’ or -C(=O)O-R’’ wherein R’’ is a linear branched or cyclic alkyl group.

The term “aryl” is understood as comprising any group comprising at least one aromatic group such as phenyl, indenyl, indanyl, benzodioxolyl, dihydrobenzodioxinyl, tetrahydronaphthalenyl or naphthalenyl group.

It is understood that by “… hydrocarbon group ...” it is meant that said group consists of hydrogen and carbon atoms and can be in the form of an aliphatic hydrocarbon, i.e. linear or branched saturated hydrocarbon (e.g. alkyl group), a linear or branched unsaturated hydrocarbon (e.g. alkenyl or alkynyl group), a saturated cyclic hydrocarbon (e.g. cycloalkyl) or an unsaturated cyclic hydrocarbon (e.g. cycloalkenyl or cycloalkynyl), or can be in the form of an aromatic hydrocarbon, i.e. aryl group, or can also be in the form of a mixture of said type of groups, e.g. a specific group may comprise a linear alkyl, a branched alkenyl (e.g. having one or more carbon-carbon double bonds), a (poly)cycloalkyl and an aryl moiety, unless a specific limitation to only one type is mentioned. Similarly, in all the embodiments of the invention, when a group is mentioned as being in the form of more than one type of topology (e.g. linear, cyclic or branched) and/or being saturated or unsaturated (e.g. alkyl, aromatic or alkenyl), it is also meant a group which may comprise moieties having any one of said topologies or being saturated or unsaturated, as explained above. Similarly, in all the embodiments of the invention, when a group is mentioned as being in the form of one type of saturation or unsaturation, (e.g. alkyl), it is meant that said group can be in any type of topology (e.g. linear, cyclic or branched) or having several moieties with various topologies.

It is understood that with the term “… a hydrocarbon group, optionally comprising one or more oxygen atoms…” it is meant that said hydrocarbon group optionally comprises one, two, three or more oxygen atoms in a form of alcohol, ketone, aldehyde, ether, ester, carboxylic acid, carbonate groups. These groups can either substitute a hydrogen atom of the hydrocarbon group and thus be laterally attached to said hydrocarbon, or substitute a carbon atom (if chemically possible) of the hydrocarbon group and thus be inserted into the hydrocarbon chain. For example, a -CH2-CH2-CHOH-CH2- group represents a C4

hydrocarbon group comprising an alcohol group (substitution of a hydrogen atom), i.e. a C4 hydrocarbon comprising an oxygen atom; a -CH2-CH2-COO-CH2-CH2CH2-CH2- group represents a C7 hydrocarbon group comprising one ester group (substitution of carbon atoms/insertion into the hydrocarbon chain), i.e. a C7 hydrocarbon comprising two oxygen atoms and, similarly, a -CH2-CH2-O-CH2-CH2-O-CH2-CH2- group represents a C6 hydrocarbon group comprising two ether groups, i.e. a C6 hydrocarbon comprising two oxygen atoms.

For the sake of clarity, by the expression “any one of its stereoisomers or a mixture thereof”, or the similar, it is meant the normal meaning understood by a person skilled in the art, i.e. that the compound of formula (I) can be a pure enantiomer or diastereomer. In other words, the compound of formula (I) may possess several stereocenters and each of said stereocenter can have two different stereochemistries (e.g. R or S). The compound of formula (I) may even be in the form of a pure enantiomer or in the form of a mixture of enantiomers or diastereoisomers. The compound of formula (I) can be in a racemic form or scalemic form. Therefore, the compound of formula (I) can be one stereoisomer or in the form of a composition of matter comprising, or consisting of, various stereoisomers.

For the sake of clarity, by the expression “each independently” it is herein understood, that each functional group to which the expression is referring to can independently be from each other one of the defined functionalities.

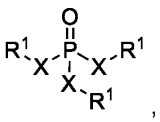
In a particular embodiment, each “each independently” can be understood as comprising different or the same functionalities, preferably as comprising the same functionalities.

For the sake of clarity, the bond marked with “*” is understood as the direct connection of the Y moiety to the R^4 moiety. In other words, the * is understood to represent the R^4 moiety when being used in the context with Y.

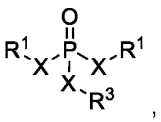
According to an embodiment, the term “polymerization reaction” refers to a chemical process in which monomers undergo a reaction to form polymer chains or networks. This includes homopolymerization, wherein identical monomer units react to form a polymer consisting of repeating units of a single type, and copolymerization, wherein two or more different types of monomers react to form a polymer with varying structural units. The polymerization reaction may proceed through various mechanisms, including but not limited to free-radical, ionic, coordination, or step-growth polymerization, depending on the monomers and reaction conditions employed.

In an embodiment the phosphorous compound of formula (I) and/or phosphorous compound of formula (II) and/or phosphorous compound of formula (III) may be preferably a phosphorous compound of formula (I) and/or phosphorous compound of formula (II), most preferably a phosphorous compound of formula (I).

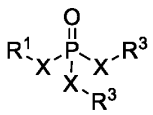
In an embodiment, the phosphorous compound of formula (I) and/or phosphorous compound of formula (II) and/or phosphorous compound of formula (III) may be one of the following:



Formula (Ia)



Formula (IIa)



Formula (IIIa)

In an embodiment, X, each independently, represents O and/or N-R^2, preferably O.

In an embodiment, R^1, each independently, represents R^4-Y_n with n representing an integer from 1 to 4, preferably n is 1 to 3, more preferably n is 1 to 2.

In an embodiment, R^2, each independently, represent H or a C_1 to C_{10} hydrocarbon moiety, optionally comprising one or more O, S and/or N atoms.

In an embodiment, R^2, each independently, represent H or a C_1 to C_{10} hydrocarbon moiety, more preferably H.

In an embodiment, R^3, each independently, represent H, Na^+, K^+, or a C_1 to C_{10} hydrocarbon moiety, optionally comprising one or more O, S and/or N atoms.

In an embodiment, R^3, each independently, represent a C_1 to C_{10} hydrocarbon moiety, more preferably C_1 to C_5 hydrocarbon moiety, more preferably C_1 to C_3 hydrocarbon moiety.

In an embodiment, R^3, each independently, represent a C_1 to C_{10} alkyl or alkenyl group, more preferably C_1 to C_3 alkyl or alkenyl group, more preferably methyl, ethyl, propyl or isopropyl group, most preferably ethyl group.

In an embodiment, R^4, each independently, represents a C_1 to C_{18} hydrocarbon moiety, optionally comprising one or more O, S and/or N atoms.

In an embodiment, R^4, each independently, represents a C_1 to C_{15} hydrocarbon moiety, optionally comprising one or more O, S and/or N atoms.

In an embodiment, R^4, each independently, represents a C_1 to C_{12} hydrocarbon moiety, optionally comprising one or more O, S and/or N atoms.

In an embodiment, R^4, each independently, represents a C_1 to C_{10} hydrocarbon moiety, optionally comprising one or more O, S and/or N atoms.

In an embodiment, R^4, each independently, represents a C_1 to C_8 hydrocarbon moiety, optionally comprising one or more O, S and/or N atoms.

In an embodiment, R^4, each independently, represents a C_1 to C_{18} hydrocarbon moiety, optionally comprising one or more O and/or N atoms, preferably optionally one or more O atoms.

In an embodiment, R^4, each independently, represents a C_1 to C_{15} hydrocarbon moiety, optionally comprising one or more O and/or N atoms, preferably optionally one or more O atoms.

In an embodiment, R^4, each independently, represents a C_1 to C_{12} hydrocarbon moiety, optionally comprising one or more O and/or N atoms, preferably optionally one or more O atoms.

In an embodiment, R^4, each independently, represents a C_1 to C_{10} hydrocarbon moiety, optionally comprising one or more O and/or N atoms, preferably optionally one or more O atoms.

In an embodiment, R^4, each independently, represents a C_1 to C_8 hydrocarbon moiety, optionally comprising one or more O and/or N atoms, preferably optionally one or more O atoms.

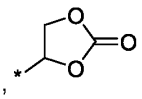
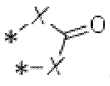
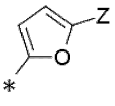
In an embodiment, R^4, each independently, represents C_6 to C_{10} aryl group, optionally substituted with one or more C_1 to C_4 alkoxy groups, preferably one or more methoxy or ethoxy groups, and/or carboxy group, or a C_1 to C_{10} linear or branched alkyl group, optionally substituted with one or more C_1 to C_4 alkoxy groups.

In an embodiment, R^4, each independently, represents C_6 aryl group, optionally substituted with one or more C_1 to C_4 alkoxy groups, and/or carboxy group, preferably one or more methoxy or ethoxy groups, or a C_1 to C_6 linear or branched alkyl group, optionally substituted with one or more C_1 to C_4 alkoxy groups.

In an embodiment, R^4, each independently, represents phenyl group, optionally substituted with one or more C_1 to C_4 alkoxy groups, and/or carboxy group, preferably one or more methoxy or ethoxy groups, or a C_1 to C_4 linear or branched alkyl group, optionally substituted with one or more C_1 to C_4 alkoxy groups.

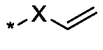
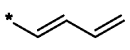
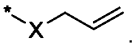
In an embodiment, Y, each independently, represents

- -OH, -NHR^2, -CHO, -NCO, and/or -COCl;
- a strained heterocycle of the following structures:

, a 5- membered ring comprising  and/or 

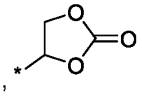
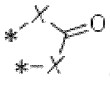
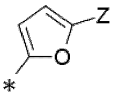
wherein Z is H or –CHO; and/or

- one of the following olefins:

, , and/or .

In an embodiment, Y, each independently, represents

- -OH, -CHO, and/or -COCl;
- a strained heterocycle of the following structures:

, a 5- membered ring comprising  and/or 

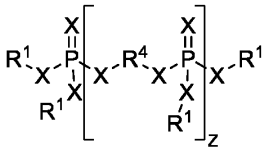
wherein Z is H or –CHO.

In an embodiment, the compound of formula (I) to (III) is selected from the group consisting of tris(4-formylphenyl) phosphate, tris(4-formyl-2-methoxyphenyl) phosphate, triallyl 3,3',3''-((oxo-λ^5-phosphanetriyl)tris(oxy))tribenzoate, tris(3-chlorocarbonylphenyl) phosphate, tris(3-formylphenyl) phosphate, tris(3-hydroxypropyl) phosphate, 3-[bis(3-acetoxypropoxy)phosphoryloxy]propyl acetate, tris(2-ethoxy-4-formyl-phenyl) phosphate, tris(2,2-dimethyl-3-oxo-propyl) phosphate, tris(3-oxopropyl) phosphate, tris(2-vinyloxyethyl) phosphate, tris[(2-oxo-1,3-dioxolan-4-yl)methyl] phosphate, ethyl bis(4-formyl-2-methoxy-phenyl) phosphate, tris(5-formyl-2-methoxy-phenyl) phosphate, tris[(5-formyl-2-furyl)methyl] phosphate, tris(5-oxopentyl) phosphate, ethyl bis(3-formylphenyl) phosphate, ethyl bis(4-formylphenyl) phosphate, tris[4-(2,5-dioxopyrrol-1-yl)phenyl] phosphate, tris[2-formylphenyl] phosphate, sodium bis(3-formylphenyl) phosphate, sodium bis(4-formylphenyl) phosphate, tris[4-aminophenyl] phosphate, 4-bis(4-formylphenoxy)phosphinothioyloxybenzaldehyde, tris[4-(5-hydroxy-1,3-dioxan-2-yl)phenyl] phosphate, tris(4-formyl-2-methyl-phenyl) phosphate, tris(4-isocyanatophenyl) thiophosphate, sodium bis(3-formylphenyl) phosphate, tris[4-(2,5-dioxopyrrol-1-yl)phenyl] phosphate, tris(4-formyl-2-methylphenyl) phosphate, tris(4-(3-hydroxypropyl)-2-methoxyphenyl) phosphate, tris(4-(3-hydroxypropyl)-2,6-dimethoxyphenyl) phosphate, and mixtures thereof.

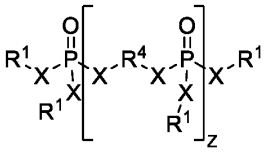
In a particular embodiment, when X-R^1 and/or X-R^2, each independently, comprises a phenol moiety, the pKa of the corresponding monomer H-X-R^1 and/or H-X-R^2, each

independently, is between 6 and 11, more preferably between 7 and 10, even more preferably between 7.5 and 9.

In an embodiment, the compounds of formula (I) to (III) are polymerized to a structure as for example following formula (IV) or more specifically (IVa):



(IV)

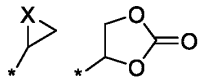
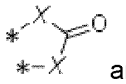
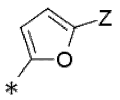


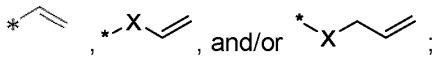
(IVa)

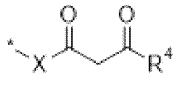
wherein the definitions for X, R^1 and R^4 are as defined herein-above for phosphorous compounds of formula (I) to (III) and Z is an integer of at least 1, preferably 1 to 50.

According to an embodiment, when the at least one phosphorous compound is a compound of formula (III), Y, each independently, represents

- a strained heterocycle of the following structures:

, a 5- or 6- membered ring comprising  and/or  wherein Z is H or –CHO;
- a free-radical polymerizable function like (meth)acrylates and/or (meth)acrylamides and/or maleimide;
- one of the following olefins:

; and/or
- one of the following malonate functions:

.

According to an embodiment, when the at least one phosphorous compound is a compound of formula (III), Y with regard to formula (III) does not represent OH, -SH, $-NHR^2$, -CHO, -NCO and/or –COCl.

Polyfunctional monomer (polyfunctional monomer A)

In an embodiment, the core-shell microcapsule comprises a shell obtainable from a polymerization reaction of at least one of the phosphorous compounds of formula (I)-(III) and at least one polyfunctional monomer, preferably a polymerisation compatible polyfunctional monomer.

The expressions “polyfunctional monomer, preferably a polymerisation compatible polyfunctional monomer” and “polyfunctional monomer A” are herein used interchangeably.

By the expression “polymerisation compatible polyfunctional monomer” it is herein understood that the polyfunctional monomer has functional groups that are polymerizable with the functional groups Y of the phosphorous compound.

For example, when the phosphorous compound comprises an electrophilic functional group Y such as –CHO, the polyfunctional monomer is polymerisation compatible in the sense that it comprises nucleophilic functional groups such as nucleophilic enol or phenol carbon groups.

For another example, when the phosphorous compound comprises an electrophilic functional group Y such as –NCO or an acyl chloride, the polyfunctional monomer is polymerisation compatible in the sense that it comprises nucleophilic functional groups such as –OH, amino groups or the like.

In an embodiment, the polyfunctional monomer is a nucleophilic polyfunctional monomer.

In an embodiment, the nucleophilic polyfunctional monomer comprises nucleophilic nitrogen groups, nucleophilic sulfur groups, nucleophilic enol or phenol carbon groups, nucleophilic oxygen groups, nucleophilic phosphor groups or mixtures thereof.

In an embodiment, the nucleophilic polyfunctional monomer comprises alcohol groups, amine groups, thiol groups, or nucleophilic enol or phenol carbon groups or mixtures thereof.

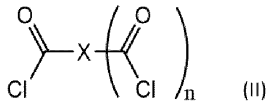
In an embodiment, the polyfunctional monomer is selected from the group consisiting of phloroglucinol, resorcinol, gallic acid, cardanol, propyl gallate and mixture thereof, preferably the polyfunctional monomer is phloroglucinol.

In an embodiment, the polyfunctional monomer is an electrophilic polyfunctional monomer.

In an embodiment, the polyfunctional monomer comprises electrophilic acyl groups, preferably acyl chloride groups, isocyanate groups, anhydride groups, aldehyde groups, epoxy groups or mixtures thereof.

In a particular embodiment, the polyfunctional monomer is an acyl chloride.

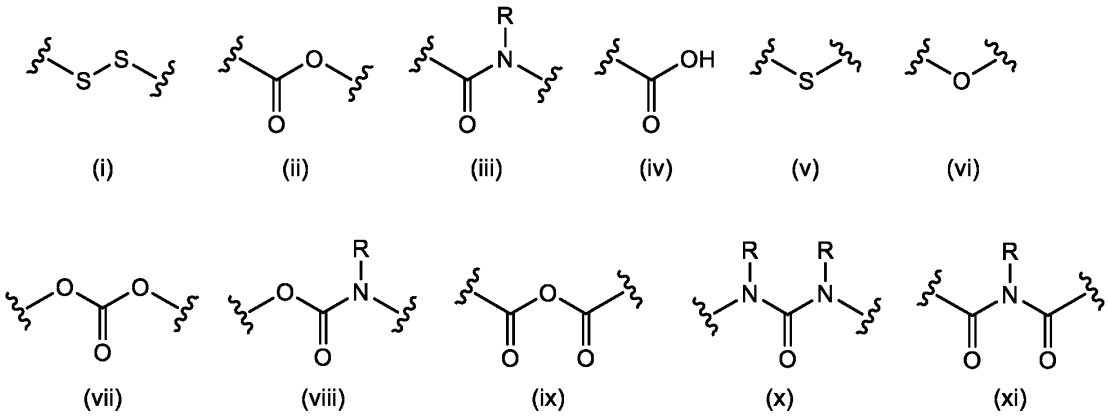
According to an embodiment, the acyl chloride has the following formula (II)



(II)

wherein n is an integer varying between 1 and 8, preferably between 1 and 6, more preferably between 1 and 4, and

wherein X is an (n+1)-valent C_2 to C_{45} hydrocarbon group optionally comprising at least one group selected from (i) to (xi),



(i) (ii) (iii) (iv) (v) (vi)

(vii) (viii) (ix) (x) (xi)

wherein R is a hydrogen atom or an alkyl group, preferably a hydrogen atom.

In a particular embodiment, the acyl chloride is chosen from the group consisting of benzene-1,3,5-tricarbonyl trichloride (trimesoyl chloride), benzene-1,2,4-tricarbonyl trichloride, benzene-1,2,4,5-tetracarbonyl tetrachloride, cyclohexane-1,3,5-tricarbonyl trichloride, isophthalyol dichloride, diglycolyl dichloride, terephthaloyl chloride, fumaryl dichloride, adipoyl dichloride, succinic dichloride, propane-1,2,3-tricarbonyl trichloride, cyclohexane-1,2,4,5-tetracarbonyl tetrachloride, 2,2'-disulfanediyldisuccinyl dichloride, 2-(2-chloro-2-oxo-ethyl)sulfanylbutanedioyl dichloride, (4-chloro-4-oxobutanoyl)-L-glutamoyl dichloride, (S)-4-((1,5-dichloro-1,5-dioxopentan-2-yl)amino)-4-oxobutanoic acid, 2,2-bis[(4-chloro-4-oxo-butanoyl)oxymethyl]butyl 4-chloro-4-oxo-butanoate, [2-[2,2-bis[(4-chloro-4-oxo-butanoyl)oxymethyl]butoxymethyl]-2-[(4-chloro-4-oxo-butanoyl)oxymethyl]butyl] 4-chloro-4-oxo-butanoate, 2,2-bis[(2-chlorocarbonylbenzoyl)oxymethyl]butyl 2-chlorocarbonyl-benzoate, [2-[2,2-bis[(2-chlorocarbonylbenzoyl)oxymethyl]butoxymethyl]-2-[(2-chlorocarbonylbenzoyl)oxymethyl]butyl] 2-chlorocarbonylbenzoate, 4-(2,4,5-

trichlorocarbonylbenzoyl)oxybutyl 2,4,5-trichlorocarbonyl-benzoate, propane-1,2,3-triyl tris(4-chloro-4-oxobutanoate), propane-1,2-diyl bis(4-chloro-4-oxobutanoate) and mixtures thereof.

In another particular embodiment, the acyl chloride is chosen from the group consisting of fumaryl dichloride, adipoyl dichloride, succinic dichloride, propane-1,2,3-triyl tris(4-chloro-4-oxobutanoate), propane-1,2-diyl bis(4-chloro-4-oxobutanoate), and mixtures thereof.

In an embodiment, the acyl chloride is a mixture of acyl chlorides.

The weight ratio between acyl chloride and the hydrophobic material is preferably comprised between 0.005 and 0.5, more preferably between 0.01 and 0.07.

In an embodiment, the acyl chloride is used in a concentration between 0.05 % to 50 %, preferably between 0.1 to 15%, by weight based on the oil phase (or hydrophobic material).

In a particular embodiment, the polyfunctional monomer is a polyisocyanate having at least two isocyanate functional groups.

Suitable polyisocyanates used according to the invention can 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 group) is used.

In 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.

In 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.

In 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. Other preferred aliphatic polyisocyanates are L-lysine diisocyanate ethyl ester.

In one embodiment, the polyfunctional monomer comprises epoxy groups.

In an embodiment, the polyfunctional monomer comprises a radical polymerisable group.

In an embodiment, the polyfunctional monomer comprises a reactive olefinic group.

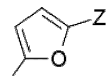
In an embodiment, the polyfunctional monomer comprises vinyl groups, allyl groups, butadienyl groups, acrylate groups or mixtures thereof.

In an embodiment, the polyfunctional monomer comprises a silane group.

In an embodiment, the polyfunctional monomer comprises alkoxysilane groups.

In an embodiment, the polyfunctional monomer comprises furfuryl groups.

In an embodiment, the polyfunctional monomer comprises maleimide groups.

In an embodiment, the at least one phosphorous compound of formula (I) and/or (II) and/or (III), wherein Y, each independently, represents –CHO or  wherein Z is –CHO, and at least one polyfunctional monomer comprising nucleophilic nitrogen groups, nucleophilic enol or phenol carbon groups, preferably phenol carbon groups, preferably wherein the polyfunctional monomer is phloroglucinol.

In an embodiment, the at least one phosphorous compound of formula (I) and/or (II) and/or (III), wherein Y, each independently, represents –OH or -NHR^2, and at least one polyfunctional monomer comprising electrophilic groups, preferably the polyfunctional monomer comprises electrophilic acyl groups, preferably epoxy groups, acyl chloride groups or isocyanate groups.

Additional polyfunctional monomers (polyfunctional monomer B)

In an embodiment, the core-shell microcapsule comprises a shell obtainable from a polymerization reaction of at least one of the phosphorous compounds of formula (I) to (III) and at least one polyfunctional monomer, preferably a polymerisation compatible polyfunctional monomer, and an additional polyfunctional monomer, preferably polyfunctional monomer having the same polymerizable groups as the phosphorous compounds of formula (I) to (III).

The expressions “polyfunctional monomer, preferably polyfunctional monomer having the same polymerizable groups as the phosphorous compounds of formula (I) to (III)” and “polyfunctional monomer B” are herein used interchangeably.

By the expression “polyfunctional monomer having the same polymerizable groups as the phosphorous compounds of formula (I) to (III)” it is herein understood that the additional polyfunctional monomer has the same polymerizable functional groups as the phosphorous compounds of formula (I) to (III).

For example, when the phosphorous compound comprises an electrophilic functional group Y such as -CHO, the additional polyfunctional monomer B comprises an electrophilic functional group Y such as –CHO so that the polyfunctional monomer A comprising for example nucleophilic carbon phenol groups can react with the –CHO functional groups of the phosphorous compound and the additional polyfunctional monomer B.

In an embodiment, the additional polyfunctional monomer B is selected from the group of 4-formylphenyl-4-formylbenzoate, bis(4-formylphenyl) succinate, succindialdehyde, adipaldehyde, glutaraldehyde, glyoxal, malondialdehyde, oleocanthal, oxidized saccharide, isophthaldehyde, and terephthaldehyde.

In an embodiment, the additional polyfunctional monomer B is selected from the group of 4-formylphenyl-4-formylbenzoate, bis(4-formylphenyl) succinate, succindialdehyde, adipaldehyde, malondialdehyde, isophthaldehyde, and terephthaldehyde.

In an embodiment, the additional polyfunctional monomer B is selected from the group of 4-formylphenyl-4-formylbenzoate, bis(4-formylphenyl) succinate, and terephthaldehyde.

Biodegradable shell material

In a particular embodiment, the shell material is a biodegradable material.

In a particular embodiment, the shell has a biodegradability of at least 40%, preferably at least 45%, 50%, 60%, 65%, 70%, 75%, 80%, 85%, 90%, 95% or 98%, within 60 days according to OECD301F.

In a particular embodiment, the core-shell microcapsule has a biodegradability of at least 40 %, preferably at least 60 %, preferably at least 65%, 70%, 75%, 80%, 85%, 90%, 95% or 98% within 60 days according to OECD301F.

Thereby it is understood that the core-shell microcapsule including all components, such as the core, shell and optionally coating may have a biodegradability of at least 40 %, preferably at least 60 %, preferably at least 65%, 70%, 75%, 80%, 85%, 90%, 95% or 98% within 60 days according to OECD301F.

In a particular embodiment, the oil core, preferably perfume oil, has a biodegradability of at least 40 %, preferably at least 60 %, preferably at least 65%, 70%, 75%, 80%, 85%, 90%, 95% or 98% within 60 days according to OECD301F.

OECD301F is a standard test method on the biodegradability from the Organization of Economic Co-operation and Development.

A typical method for extracting the shell for measuring the biodegradability is disclosed in Gasparini and all in Molecules 2020, 25,718.

Outer coating

According to a particular embodiment of the invention, the microcapsule comprises an outer coating, wherein the outer coating comprises a coating material selected from the group consisting of a non-ionic polysaccharide, a cationic polymer, a polysuccinimide derivative (as described for instance in WO2021185724), an anionic polymer and mixtures thereof to form an outer coating to the microcapsule.

Non-ionic polysaccharide polymers are well known to a person skilled in the art and are described for instance in WO 2012/007438 page 29, lines 1 to 25 and in WO 2013/026657 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.

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 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 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 hydroxypropyltrimonium chloride and cellulose hydroxypropyltrimonium chloride. Preferably copolymers shall be selected from the group consisting of polyquaternium-5, polyquaternium-6, polyquaternium-7, polyquaternium10, polyquaternium-11, polyquaternium-16, polyquaternium-22, polyquaternium-28, polyquaternium-43, polyquaternium-44, polyquaternium-46, cassia hydroxypropyltrimonium chloride, guar hydroxypropyltrimonium chloride or 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).

Anionic polymers are well known to a person skilled in the art. Preferred anionic polymers have anionic 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 anionic charge density of the anionic polymers may be determined by standard titration methods, such as polyelectrolyte titration using a cationic titrant. The preferred anionic polymers are chosen from those that contain units comprising carboxylate, sulfonate, sulfate, or phosphate groups, which 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 anionic polymer is preferably between 10,000 and 3.5M Dalton, more preferably between 50,000 and 1.5M Dalton.

According to an embodiment, the anionic polymer is selected from the group consisting of carboxymethylcellulose and salts thereof, anionic modified starch and salts thereof, gum Arabic and salts thereof, pectin and salts thereof, alginate and salts thereof, carrageenan and salts thereof, polyvinyl alcohol and salts thereof, polyaspartate and salts thereof and mixtures thereof.

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. 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.

According to a particular embodiment, the microcapsule of the present invention comprises a mineral layer. The mineral layer preferably comprises a material chosen in the group consisting of iron oxides, iron oxyhydroxide, titanium oxides, zinc oxides, calcium carbonates, calcium phosphates, barium salt, strontium salt, magnesium salt, and mixtures thereof and mixtures thereof.

Coacervate structure

In an embodiment, the shell comprises a coacervate or coacervate-like structure comprising as first polyelectrolyte and a second polyelectrolyte.

A coacervate structure is formed by a phase-separation process of polymers and is formed by the spontaneous aggregation of macromolecules/polymers (mainly due to electrostatic interactions, hydrogen bonding, or hydrophobic effects among polymer chains).

A coacervate-like structure exhibits polymer aggregation by forming a crosslinked network among polymer chains (such as crosslinked polymer layer) via physical interactions (electrostatic interactions, hydrogen bonding), but also via additional chemical cross-linkage (with chemical crosslinker or enzyme).

In a particular embodiment, the coacervate or coacervate-like structure comprises a first polyelectrolyte, preferably is selected from the group consisting of gum arabic, modified starch, pectin, carboxymethyl cellulose, sodium carboxymethyl guar gum, carrageenan, lignin, plant gums, glycogen, polyaspartate, proteins and mixtures thereof and a second polyelectrolyte, preferably is selected from the group consisting of poly(L-lysine), animal proteins, gelatin, casein, plant proteins, chitin, chitosan, silk protein and mixtures thereof.

In a particular embodiment, the pectin is selected from the group consisting of high methoxy pectin, low methoxy pectin, sugar beet pectin and mixtures thereof.

The coacervate material can be either hardened by the inventive process during the curing step and/or by adding a suitable cross-linker such as glutaraldehyde, glyoxal, formaldehyde, tannic acid or genipin or can be hardened enzymatically using an enzyme.

Method of the invention

The present invention also relates to a process for preparing a core-shell microcapsule comprising the steps of:

a) Dispersing an oil phase comprising a hydrophobic material into a continuous phase C1 to form a two-phases dispersion;
b) Optionally, dispersing the two-phases dispersion into a continuous phase C2 to form a multiple dispersion,
c) curing the dispersion obtained in step a) or in step b) to form microcapsules in the form of a slurry,
wherein a phosphorous compound of formula (I) and/or formula (II), and/or formula (III) is added in the continuous phase(s) and/or in the oil phase and
optionally, wherein a polyfunctional monomer is added in the continuous phase(s) and/or in the oil phase.

The embodiments disclosed for the core-shell microcapsules also apply for the process for preparing core-shell microcapsules. It applies notably to the phosphorous compound of formula (I) to (III), the polyfunctional monomer and the hydrophobic material.

In an embodiment, the continuous phase C1 and/or C2, each independently, comprises, preferably consists of water.

In an embodiment, the continuous phase C1 and/or C2, each independently, is a water phase.

In an embodiment, the two-phases dispersion is an oil-in-water emulsion.

In an embodiment, the continuous phase C1 and/or C2, each independently, comprises water and an alcohol such as glycerol, 1,4-butanediol, propane diols, such as 1,3-propane diol or 1,2-propane diol, ethylene glycol and mixtures thereof.

In an embodiment, the continuous phase C1 and/or C2, each independently, consists of alcohol.

In an embodiment, the multiple dispersion is a two-phases dispersion, preferably an oil-in-water emulsion.

In an embodiment, a stabilizer is added in the oil phase and/or in the continuous phase C1 and/or C2.

In a particular embodiment, the stabilizer is added in the continuous phase C1 and/or C2.

By “stabilizer”, it is meant a compound capable to stabilize oil/dispersing phase interface (typically oil/water interface) as an emulsion.

The stabilizer is preferably used in an amount comprised between 0.05% to 20 %, preferably between 0.1 to 10%, even more preferably between 0.5 and 5% by weight based on the two-phases dispersion, preferably oil-in-water emulsion.

"Stabilizer" or "emulsifier" can be used indifferently in the present invention.

In an embodiment, the stabilizer is a colloidal stabilizer.

The colloidal stabilizer can be a polymeric emulsifier (standard emulsion), a surfactant, or solid particles (Pickering emulsion).

By "polymeric emulsifier", it meant an emulsifier having both a polar group with an affinity for water (hydrophilic) and a nonpolar group with an affinity for oil (hydrophobic). The hydrophilic part will dissolve in the water phase and the hydrophobic part will dissolve in the oil phase providing a film around droplets.

By "surfactant", it meant a substance with a polar and a non-polar group that is added to the liquid to reduce the liquid surface tension.

In an embodiment, the stabilizer is chosen in the group consisting of inorganic particles, polymeric particles, polymeric emulsifier such as polysaccharides, proteins, glycoproteins, and mixtures thereof.

When the stabilizer is solid particles, it can be chosen in the group consisting of calcium phosphate, silica, silicates, titanium dioxide, aluminium oxide, zinc oxide, iron oxide, mica, kaolin, montmorillonite, laponite, bentonite, perlite, dolomite, diatomite, vermiculite, hectorite, gibbsite, illite, kaolinite, aluminosilicates, gypsum, bauxite, magnesite, talc, magnesium carbonate, calcium carbonate, diatomaceous earth and mixtures thereof.

When the stabilizer is polymer particles, it can be chosen in the group consisting of starch particles, lignin particles, silk fibroin particles, zein particles, gliadin particles, coacervate particles comprising a first polymer and a second polymer, and mixtures thereof.

In a particular embodiment, the stabilizer is a biopolymer.

By "biopolymers" it is meant biomacromolecules produced by living organisms. Biopolymers are characterized by molecular weight distributions ranging from 1,000 (1 thousand) to 1,000,000,000 (1 billion) Daltons. These macromolecules may be carbohydrates (sugar based) or proteins (amino-acid based) or a combination of both (gums) and can be linear or branched.

In an embodiment, the polymeric emulsifier is chosen in the group consisting of gum Arabic, modified starch, polyvinyl alcohol, polyvinylpyrolidone (PVP), carboxymethylcellulose (CMC), anionic polysaccharides, sodium polyaspartate, acrylamide copolymer, protein such as soy protein, rice protein, whey protein, white egg albumin, sodium caseinate, gelatin, bovine serum albumin, hydrolyzed soy protein, hydrolyzed sericin, pseudocollagen, silk protein, sericin powder, potato protein, chickpea protein, pea protein, algae protein, faba bean protein, barley protein, oat protein, wheat gluten protein, lupin protein, and mixtures thereof.

Potato proteins are typically extracted from potato tuber (Solanum tuberosum). According to an embodiment, the potato protein is a native potato protein and preferably patatin.

In an embodiment, the stabilizer is selected from the group consisting of inorganic particles, surfactant, polymeric emulsifier such as polysaccharides, proteins, glycoproteins and mixtures thereof.

In an embodiment, the polyfunctional monomer is added in the oil phase or in the continuous phase C1 and/or C2.

In a particular embodiment, the polyfunctional monomer is added to the continuous phase C1 and/or C2.

The polyfunctional monomer, as defined previously, is preferably used in an amount comprised between 0.01% and 30%, preferably between 0.1% and 10%, preferably between 0.5 and 5% based on the total weight of the two-phases dispersion, preferably oil-in-water emulsion.

In an embodiment, the polyfunctional monomer is added in an amount comprised between 0.1 and 10%, preferably between 0.2 and 4.0 % by weight, based on the total weight of the two-phases dispersion, preferably oil-in-water emulsion.

In an embodiment, the phosphorous compound of formula (I) to (III) is added in the oil phase or in the continuous phase C1 and/or C2.

In a particular embodiment, the phosphorous compound of formula (I) to (III) is added in the oil phase.

Any compound of formula (I) and/or formula (II) and/or formula (III) can be used in an amount comprised between 0.01% and 30%, preferably between 0.05% and 8%, more preferably between 0.5 and 5% based on the total weight of the two phases dispersion, preferably oil-in-water emulsion.

In an embodiment, any compound of formula (I) and/or formula (II) and/or formula (III) is added in an amount comprised between 0.01% and 10%, preferably between 0.5% and 5%, more preferably between 1% and 3% by weight, based on the total weight of the two-phases dispersion, preferably oil-in-water emulsion.

In an embodiment, at least one salt is added in the dispersing phase and/or in the oil phase and/or in the two-phases dispersion.

The salt is preferably used in an amount comprised between 0.01% and 10% by weight based on the two-phases dispersion.

The salt added in the aqueous phase can be chosen in the group consisting of calcium, zinc, sodium, potassium, lithium, magnesium, aluminum, iron, manganese, copper, titanium,

barium, sulphates, phosphates, nitrates, bromides, chlorides, iodides, acetates, and ammonium salts.

In an embodiment, the salt is chosen in the group consisting of $CaCl_2$, NaCl, KCl, $ZnCl_2$, $ZnSO_4$, $Zn(NO_3)_2$, LiCl, $Ca(NO_3)_2$, $MgCl_2$, $CaBr_2$, CaI_2, NaBr, NaI, $NaNO_3$, KBr, KI, KNO_3, LiBr, LiI, $MgBr_2$,$CuCl_2$, $FeCl_2$, $FeCl_3$, $TiCl_4$, $MnCl_2$, and mixtures thereof.

The pH of the dispersing phase is preferably comprised between 2 and 12, preferably between 3 and 8, more preferably between 3 and 5.

In an embodiment, a base is added in step a) and/or b).

In a particular embodiment, the base is selected from the group consisting of guanidine carbonate, sodium carbonate, potassium carbonate, sodium hydroxide or mixtures thereof.

In an embodiment, an acid is added in step a) and/or b).

In a particular embodiment, the acid is selected from the group consisting of formic acid, acetic acid, HCl or nitric acid or mixtures thereof.

In an embodiment, the pH is adjusted in step a) and/or b) to a pH value from 2 to 9, preferably to a pH value from 2.5 to 7, more preferably to a pH value from 3.0 to 6.5.

In an embodiment, the curing in step c) is performed in a temperature range of 20 to 90°C, preferably 50 to 88°C, more preferably 70 to 85°C.

In an embodiment, the curing in step c) is performed over a time period from 1 h to 24 h, preferably over a time period from 2 h to 18 h, more preferably over a time period from 3 h and 16 h, more preferably over a time period from 4 to 12 h.

In an embodiment, the process comprises an optional step after the curing step c) (i.e. step d) of adding a solution of a stabilizer, preferably an anionic colloidal stabilizer or a first polyelectrolyte.

In an embodiment, a solution of a stabilizer, preferably an anionic colloidal stabilizer or a first polyelectrolyte, is an aqueous solution.

In an embodiment, the solution of a stabilizer is added at about the curing temperature of step c), such as in a temperature range of 20 to 90°C, preferably 50 to 88°C, more preferably 70 to 85°C.

In an embodiment, the process comprises an optional step after the curing step c) and/or step d) (i.e. step e) of adjusting, preferably cooling down, the dispersion to a temperature comprised between 0 and 70°C, preferably 5 to 60°C, more preferably 10 to 40°C.

In an embodiment, the adjustment, preferably cooling down, is achieved by air cooling or cooling with cooling means, such as ice cooling.

In an embodiment, the process comprises an optional step after the curing step c) and/or step d) and/or step e) (i.e. step f) of adding a second polyelectrolyte, preferably a cationic polymer, preferably to form a coacervate.

In an embodiment, the process steps d) and f) are mandatory in order to form the coacervate.

In an embodiment, the process comprises an optional step after the curing step c) and/or step d) and/or step e) and/or step f) (step g) of additional curing the mixture.

In an embodiment, the curing in step g) is performed in a temperature range of 20 to 90°C, preferably 40 to 88°C, more preferably 50 to 70°C.

In an embodiment, the curing in step g) is performed over a time period from 10 min to 12 h, preferably over a time period from 30 min to 4 h, more preferably over a time period from 45 min and 2 h.

In an embodiment, the process comprises a further optional step after the curing step g) (i.e. step h) of adding a solution of a stabilizer, preferably an anionic colloidal stabilizer or a first polyelectrolyte as described herein-above.

In an embodiment, a solution of a stabilizer, preferably an anionic colloidal stabilizer or a first polyelectrolyte, is an aqueous solution.

In an embodiment, the solution of a stabilizer is added at about the curing temperature of step c), such as in a temperature range of 20 to 90°C, preferably 40 to 88°C, more preferably 50 to 70°C.

In an embodiment, the process comprises an optional step after the curing step g) and/or step h) (i.e. step i) of adjusting, preferably cooling down, the dispersion to a temperature comprised between 0 and 70°C, preferably 5 to 60°C, more preferably 10 to 40°C, more preferably room temperature (i.e. 21°C).

In an embodiment, the adjustment, preferably cooling down, is achieved by air cooling or cooling with cooling means, such as ice cooling.

MULTIPLE MICROCAPSULES SYSTEM

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

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

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

According to a particular embodiment, the microcapsule delivery system is in the form of a slurry.

The wall of the second type of microcapsules can vary. As non-limiting examples, the polymer shell of the second type of microcapsules comprises a material selected from the group consisting of polyurea, polyurethane, polyamide, polyhydroxyalkanoates, polyacrylate, polyesters, polyaminoesters, polyepoxides, organosilicon, polycarbonate, polysulfonamide, urea formaldehyde, melamine formaldehyde resin, melamine formaldehyde resin cross-linked with polyisocyanate or aromatic polyols, melamine urea resin, melamine glyoxal resin, gelatin/ gum arabic shell wall, and mixtures thereof.

The second type of microcapsule can comprise an oil-based core comprising a hydrophobic active, preferably perfume, and a composite shell comprising a first material and a second material, wherein the first material and the second material are different, the first material is a coacervate, the second material is a polymeric material. In an embodiment, the weight ratio between the first material and the second material is comprised between 50:50 and 99.9:0.1. In an embodiment, the coacervate comprises a first polyelectrolyte, preferably selected among proteins (such as gelatin), polypeptides or polysaccharides (such as chitosan), most preferably Gelatin and a second polyelectrolyte, preferably alginate salts, cellulose derivatives guar gum, pectinate salts, carrageenan, polyacrylic and methacrylic acid or xanthan gum, or yet plant gums such as acacia gum (Gum Arabic), most preferably Gum Arabic. The coacervate first material can be hardened chemically using a suitable cross-linker such as glutaraldehyde, glyoxal, formaldehyde, tannic acid or genipin or can be hardenedenzymatically using an enzyme such as transglutaminase. The second polymeric material can be selected from the group consisting of polyurea, polyurethane, polyamide, polyester, polyacrylate, organosilicon, polycarbonate, polysulfonamide, polymers of urea and formaldehyde, melamine and formaldehyde, melamine and urea, or melamine and glyoxal and mixtures thereof, preferably polyurea and/or polyurethane. The second material is preferably present in an amount less than 3 wt.%, preferably less than 1 wt.% based on the total weight of the second type of microcapsule slurry.

As non-limiting examples, the shell of the second type of microcapsules can be aminoplast-based, polyurea-based or polyurethane-based. The shell of the second type of microcapsules 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.

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

According to another aspect the shell of the second type of microcapsules is polyurea-based made from, for example but not limited to isocyanate-based monomers and amine-containing crosslinkers such as guanidine carbonate and/or guanazole. Certain 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. However, the use of an amine can be omitted. According to a particular aspect, 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 aspect, the emulsifier is an anionic or amphiphilic biopolymer, which may be, in one aspect, chosen from the group consisting of gum Arabic, soy protein, gelatin, sodium caseinate and mixtures thereof.

According to another embodiment, the microcapsule wall material of the second type of microcapsules 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, 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.), Sigma-Aldrich (St. Louis, Missouri U.S.A.).

According to another embodiment, the second type of microcapsules is a one-shell aminoplast core-shell microcapsule obtainable by a process comprising the steps of:

1) admixing a perfume oil with at least a polyisocyanate having at least two isocyanate functional groups to form an oil phase;
2) dispersing or dissolving into water an aminoplast resin and optionally a stabilizer to form a dispersing phase;
3) preparing an oil-in-water dispersion, wherein the mean droplet size is comprised between 1 and 100 microns, by admixing the oil phase and the dispersing phase;

4) performing a curing step to form the wall of said microcapsule; and

5) optionally drying the final dispersion to obtain the dried core-shell microcapsule.

According to an embodiment, the second type of microcapsules 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:
   a. a polyamine component in the form of melamine or of a mixture of melamine and at least one C_1-C_4 compound comprising two NH2 functional groups;
   b. an aldehyde component in the form of a mixture of glyoxal, a C_{4-6} 2,2-dialkoxy-ethanal and optionally a glyoxalate, said mixture having a molar ratio glyoxal/C_{4-6} 2,2-dialkoxy-ethanal comprised between 1/1 and10/1; and
   c. a protic acid catalyst;
2) preparing an oil-in-water dispersion, wherein the droplet size is comprised between 1 and 600 microns, and comprising:
   a. an oil;
   b. a water medium:
   c. at least an oligomeric composition as obtained in step 1;
   d. at least a cross-linker selected amongst:
      i. C_4-C_{12} aromatic or aliphatic di- or tri-isocyanates and their biurets, triurets, trimmers, trimethylol propane-adduct and mixtures thereof; and/or
      ii. a di- or tri-oxiran compounds of formula:
      A-(oxiran-2-ylmethyl)$_n$
      wherein $_n$ stands for 2 or 3 and 1 represents a C_2-C_6 group optionally comprising from 2 to 6 nitrogen and/or oxygen atoms;
   e. optionally a C_1-C_4 compounds comprising two NH_2 functional groups;
3) Heating the dispersion; and
4) Cooling the dispersion.

In another particular embodiment, the second type of microcapsule comprises

- an oil-based core comprising a hydrophobic active, preferably perfume,
- optionally an inner shell made of a polymerized polyfunctional monomer;
- a biopolymer shell comprising a protein, wherein at least one protein is cross-linked.

According to a particular embodiment, the protein is chosen in the group consisting of milk proteins, caseinate salts such as sodium caseinate or calcium caseinate, casein, whey protein, hydrolyzed proteins, gelatins, gluten, pea protein, soy protein, silk protein and mixtures thereof, preferably sodium caseinate, most preferably sodium caseinate

According to a particular embodiment, the protein comprises sodium caseinate and a globular protein, preferably chosen in the group consisting of whey protein, beta-lactoglobulin, ovalbumine, bovine serum albumin, vegetable proteins, and mixtures thereof.

The protein is preferably a mixture of sodium caseinate and whey protein.

According to a particular embodiment, the biopolymer shell comprises a crosslinked protein chosen in the group consisting of sodium caseinate and/or whey protein.

According to a particular embodiment, the second type of microcapsules slurry comprises at least one microcapsule made of:

- an oil-based core comprising the hydrophobic active, preferably perfume;
- an inner shell made of a polymerized polyfunctional monomer; preferably a polyisocyanate having at least two isocyanate functional groups
- a biopolymer shell comprising a protein, wherein at least one protein is cross-linked; wherein the protein contains preferably a mixture comprising sodium caseinate and a globular protein, preferably whey protein,
- optionally at least an outer mineral layer.

According to an embodiment, sodium caseinate and/or whey protein is (are) cross-linked protein(s).

The weight ratio between sodium caseinate and whey protein is preferably comprised between 0.01 and 100, preferably between 0.1 and 10, more preferably between 0.2 and 5.

In another particular embodiment, the second type of microcapsules is a polyamide core-shell polyamide microcapsule comprising:

- an oil-based core comprising comprising a hydrophobic active, preferably perfume, and
- a polyamide shell comprising or being obtainable from:
    - an acyl chloride,
    - a first amino compound,
    - a second amino compound,
    - optionally, a carbohydrate.

According to a particular embodiment, the second type of microcapsules comprises:

- an oil-based core comprising a hydrophobic active, preferably perfume, and
- a polyamide shell comprising or being obtainable from:
    - an acyl chloride, preferably in an amount comprised between 5 and 98%, preferably between 20 and 98%, more preferably between 30 and 85% w/w
    - a first amino compound, preferably in an amount comprised between 1% and 50% w/w, preferably between 7 and 40% w/w;

- a second amino compound, preferably in an amount comprised between 1% and 50% w/w, preferably between 2 and 25% w/w
- a stabilizer, preferably a biopolymer, preferably in an amount comprised between 0 and 90%, preferably between 0.1 and 75%, more preferably between 1 and 70%,
- optionally, a carbohydrate.

According to a particular embodiment, the second type of microcapsules comprises:

- an oil-based core comprising a hydrophobic active, preferably perfume, and
- a polyamide shell comprising or being obtainable from:
  - an acyl chloride,
  - a first amino-compound being an amino-acid, preferably chosen in the group consisting of L-Lysine, L-Arginine, L-Histidine, L-Tryptophane and/or mixtures thereof.
  - a second amino-compound, preferably chosen in the group consisting of ethylene diamine, diethylene triamine, cystamine and/or mixtures thereof, and
  - a biopolymer, preferably chosen in the group consisting of potato protein, chickpea protein, pea protein, algae protein, faba bean protein, barley protein, oat protein, wheat gluten protein, lupin protein, soy protein, rice protein, whey protein, white egg albumin, casein, sodium caseinate, gelatin (preferably fish gelatin), bovine serum albumin, hydrolyzed soy protein, hydrolyzed sericin, pseudocollagen, silk protein, sericin powder, gelatin and mixtures thereof,
  - optionally a carbohydrate, preferably selected from the group consisting of anionic salt of alginic acid, preferably alginic acid sodium salt, pectin, lignin, anionic modified starch, carboxymethylcellulose, carrageenan and mixtures thereof.

According to another aspect, the shell of the second type of microcapsules is polyurea- or polyurethane-based. Examples of processes for the preparation of polyurea and polyurethane-based microcapsule slurry are for instance described in International Patent Application Publication No. WO2007/004166, European Patent Application Publication No. EP 2300146, and European Patent Application Publication No. EP25799. 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;

b) Preparing an aqueous solution of an emulsifier or colloidal stabilizer to form a dispersing phase;
c) Adding the oil phase to the dispersing 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; and
d) Applying conditions sufficient to induce interfacial polymerisation and form microcapsules in form of a slurry.

PERFUMING COMPOSITION AND CONSUMER PRODUCTS

The present invention also relates to a perfuming composition comprising

- a core-shell microcapsule or core-shell microcapsule slurry as described herein-above or obtained by the process according to the present invention,
- at least one ingredient selected from the group consisting of a perfumery carrier and a perfumery base, and
- optionally, at least one perfumery adjuvant.

In an embodiment, the composition comprises:

– a core-shell microcapsule or core-shell microcapsule slurry as described herein-above or as obtained by the process according to the present invention;
– 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.

In an embodiment, a core-shell microcapsule or core-shell microcapsule slurry as described herein-above or as obtained by the process according to the present invention can also be added in different perfumed consumer products.

In an embodiment, present invention relates to a perfuming composition comprising

- a core-shell microcapsule or core-shell microcapsule slurry as described herein-above or as obtained by the process according to the present invention and
- optionally, a free perfume oil.

Preferably, the perfuming composition according to the invention comprises between 0.1 and 40 %, preferably between 0.1 and 30% by weight of a core-shell microcapsule or core-shell microcapsule slurry as described herein-above or obtained by the process according to the present invention.

By “free perfume” it is herein understood a perfume or perfume oil which is comprised in the perfuming composition and not entrapped in the core-shell microcapsule or core-shell microcapsule slurry as described herein-above or as obtained by the process according to the present invention.

In an embodiment, the total amount of the core-shell microcapsule or core-shell microcapsule slurry as described herein-above or as obtained by the process according to the present invention is 0.05 to 5 wt.% (based on the total weight of the perfuming composition) and the total amount of the free perfume oil is 0.05 to 5 wt.% (based on the total weight of the perfuming composition).

In an embodiment, the total perfume oil of the perfume formulation entrapped in the core-shell microcapsule or core-shell microcapsule slurry as described herein-above or as obtained by the process according to the present invention and total free perfume oil are present in the perfuming composition in a weight ratio of 1:20 to 20:1, preferably 10:1 to 1:10.

The perfuming composition can further comprise at least one perfuming co-ingredient and, optionally a perfumery adjuvant.

By “perfuming co-ingredient” it is herein understood a compound, which is used in a perfuming preparation or a composition to impart a hedonic effect and which is not a microcapsule as 20 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 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, acetates, nitriles, terpenoids, nitrogenous or sulfur heterocyclic compounds and essential oils, and said perfuming co-ingredients can be of natural or synthetic origin. Many of these co-30 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 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. Co-ingredients may be chosen in the group consisting of 4-(dodecylthio)-4-(2,6,6-trimethyl-2-cyclohexen-1-yl)-2-butanone, 4-(dodecylthio)-4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2-butanone, trans-3-(dodecylthio)-1-(2,6,6-trimethyl-3-cyclohexen-1-yl)-1-butanone, 2-(dodecylthio)octan-4-one, 2-phenylethyl oxo(phenyl)acetate, 3,7-dimethylocta-2,6-dien-1-yl oxo(phenyl)acetate, (Z)-hex-3-en-1-yl oxo(phenyl)acetate, 3,7-

dimethyl-2,6-octadien-1-yl hexadecanoate, bis(3,7-dimethylocta-2,6-dien-1-yl) succinate, (2-((2-methylundec-1-en-1-yl)oxy)ethyl)benzene, 1-methoxy-4-(3-methyl-4-phenethoxybut-3-en-1-yl)benzene, (3-methyl-4-phenethoxybut-3-en-1-yl)benzene, 1-(((Z)-hex-3-en-1-yl)oxy)-2-methylundec-1-ene, (2-((2-methylundec-1-en-1-yl)oxy)ethoxy)benzene, 2-methyl-1-(octan-3-yloxy)undec-1-ene, 1-methoxy-4-(1-phenethoxyprop-1-en-2-yl)benzene, 1-methyl-4-(1-phenethoxyprop-1-en-2-yl)benzene, 2-(1-phenethoxyprop-1-en-2-yl)naphthalene, (2-phenethoxyvinyl)benzene, 2-(1-((3,7-dimethyloct-6-en-1-yl)oxy)prop-1-en-2-yl)naphthalene, (2-((2-pentylcyclopentylidene)methoxy)ethyl)benzene, 4-allyl-2-methoxy-1-((2-methoxy-2-phenylvinyl)oxy)benzene, (2-((2-heptylcyclopentylidene)methoxy)ethyl)benzene, 1-isopropyl-4-methyl-2-((2-pentylcyclopentylidene)methoxy)benzene, 2-methoxy-1-((2-pentylcyclopentylidene)methoxy)-4-propylbenzene, 3-methoxy-4-((2-methoxy-2-phenylvinyl)oxy)benzaldehyde, 4-((2-(hexyloxy)-2-phenylvinyl)oxy)-3-methoxybenzaldehyde or a mixture thereof or a mixture thereof.

By “perfumery adjuvant” it is herein understood an ingredient capable of imparting additional 5 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 exhaustive, but it has to be mentioned that said ingredients are well known to a person skilled in the art.

The core-shell microcapsule or core-shell microcapsule slurry as described herein-above or as obtained by the process according to the present invention can advantageously be used in many application fields and used in consumer products.

The present invention also relates to a perfumed consumer product comprising

- a core-shell microcapsule or core-shell microcapsule slurry as described herein-above or as obtained by the process according to the present invention, and
- a personal care, home care, or fabric care active base.

The consumer 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 home-care products including laundry care and air care.

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

- a perfuming composition or the core-shell microcapsule or core-shell microcapsule slurry as described herein-above or as obtained by the process according to the present 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
- a perfuming composition or the core-shell microcapsule or core-shell microcapsule slurry as described herein-above or as obtained by the process according to the present invention.

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 products can be a fine perfume, a splash or eau de perfume, a cologne, a shave or after-shave lotion, a liquid or solid detergent, a mono or multi chamber unidose detergent , a fabric softener, a fabric refresher, liquid or solid scent-boosters (PEG / urea or salts), a dryer sheet, an ironing water, a paper, a bleach, a carpet cleaners, curtain–care products, a shampoo, a coloring preparation, a color care product, a hair shaping product, a dental care product, a disinfectant, an intimate care product, a hair spray, a hair conditioning product, a vanishing cream, a deodorant or antiperspirant, hair remover, tanning or sun product, nail products, skin cleansing, a makeup, a perfumed soap, shower or bath mousse, oil or gel, or a foot/hand care products, a hygiene product, an air freshener, a “ready to use” powdered air freshener, a mold remover, furnisher care, wipe, a dish detergent or hard-surface detergent, a leather care product, a car care product.

In an embodiment, the perfumed consumer product is preferably selected from the group consisting of personal care composition, home care composition or fabric care composition, most preferably in form of antiperspirants, hair care products, such as shampoo or hair-conditioner, body care products such as a shower gel, oral care products, laundry care products, preferably a detergent or a fabric softener.

The present invention also relates to a consumer product comprising:

- a personal care active base, and
- microcapsules or a microcapsule slurry 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 bases 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.

The personal care composition is preferably chosen in the group consisting of a hair-care product (e.g. a shampoo, hair conditioner, a coloring 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).

The present invention also relates to a consumer product comprising:

- a home care or a fabric care active base, and
- microcapsules or a microcapsule slurry 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 active bases 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.

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.

For liquid consumer product mentioned below, by “active base”, it should be understood that the active base includes active materials (typically including surfactants).

For solid consumer product mention below, by “active base”, it should be understood that the active base includes active materials (typically including surfactants) and auxiliary agents (such as bleaching agents, buffering agent; builders; soil release or soil suspension polymers; granulated enzyme particles, corrosion inhibitors, antifoaming, sud suppressing agents; dyes, fillers, and mixtures thereof).

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

Fabric softener

An object of the invention is a consumer product in the form of a fabric softener composition comprising:

- a fabric softener active base; preferably comprising at least one active material chosen in the group consisting of dialkyl quaternary ammonium salts, dialkyl ester quaternary ammonium salts (esterquats), Hamburg esterquat (HEQ), TEAQ (triethanolamine quat), silicones and mixtures thereof, the active base being used preferably in an amount comprised between 85 and 99.95% by weight based on the total weight of the composition,
- microcapsules or a microcapsule slurry as defined above, preferably in an amount comprised between 0.05 to 15 wt%, more preferably between 0.1 and 5 wt% by weight based on the total weight of the composition,
- optionally free perfume oil.

Liquid detergent

An object of the invention is a consumer product in the form of a liquid detergent composition comprising:

- a liquid detergent active base; preferably comprising at least one active material chosen in the group consisting of anionic surfactant such as alkylbenzenesulfonate (ABS), secondary alkyl sulfonate (SAS), primary alcohol sulfate (PAS), lauryl ether sulfate (LES), methyl ester sulfonate (MES) and nonionic surfactant such as alkyl amines, alkanolamide, fatty alcohol poly(ethylene glycol) ether, fatty alcohol ethoxylate

(FAE), ethylene oxide (EO) and propylene oxide (PO) copolymers, amine oxydes, alkyl polyglucosides, alkyl polyglucosamides, the active base being used preferably in an amount comprised between 85 and 99.95% by weight based on the total weight of the composition,

- microcapsules or a microcapsule slurry as defined above, preferably in an amount comprised between 0.05 to 15 wt%, more preferably between 0.1 and 5 wt% by weight based on the total weight of the composition,
- optionally free perfume oil.

Solid detergent

An object of the invention is a consumer product in the form of a solid detergent composition comprising:

- a solid detergent active base; preferably comprising at least one active material chosen in the group consisting of anionic surfactant such as alkylbenzenesulfonate (ABS), secondary alkyl sulfonate (SAS), primary alcohol sulfate (PAS), lauryl ether sulfate (LES), methyl ester sulfonate (MES) and nonionic surfactant such as alkyl amines, alkanolamide, fatty alcohol poly(ethylene glycol) ether, fatty alcohol ethoxylate (FAE), ethylene oxide (EO) and propylene oxide (PO) copolymers, amine oxydes, alkyl polyglucosides, alkyl polyglucosamides, the active base being used preferably in an amount comprised between 85 and 99.95% by weight based on the total weight of the composition,
- a microcapsule powder or microcapsule slurry as defined above, preferably in an amount comprised between 0.05 to 15 wt%, more preferably between 0.1 and 5 wt% by weight based on the total weight of the composition,
- optionally free perfume oil.

Shampoo/shower gel

An object of the invention is a consumer product in the form of a shampoo or a shower gel composition comprising:

- a shampoo or a shower gel active base; preferably comprising at least one active material chosen in the group consisting of sodium alkylether sulfate, ammonium alkylether sulfates, alkylamphoacetate, cocamidopropyl betaine, cocamide MEA, alkylglucosides and aminoacid based surfactants and mixtures thereof, the active base being used preferably in an amount comprised between 85 and 99.95% by weight based on the total weight of the composition,

- microcapsules or a microcapsule slurry as defined above, preferably in an amount comprised between 0.05 to 15 wt%, more preferably between 0.1 and 5 wt% by weight based on the total weight of the composition,
- optionally free perfume oil.

Rinse-Off Conditioner

An object of the invention is a consumer product in the form of a rinse-off conditioner composition comprising:

- a rinse-off conditioner active base; preferably comprising at least one active material chosen in the group consisting of cetyltrimonium chloride, stearyl trimonium chloride, benzalkonium chloride, behentrimonium chloride and mixture thereof, the active base being used preferably in an amount comprised between 85 and 99.95% by weight based on the total weight of the composition,
- microcapsules or a microcapsule slurry as defined above, preferably in an amount comprised between 0.05 to 15 wt%, more preferably between 0.1 and 5 wt% by weight based on the total weight of the composition,
- optionally free perfume oil.

Solid scent booster

An object of the invention is a consumer product in the form of a solid scent booster composition comprising:

- a solid carrier, preferably chosen in the group consisting of urea, sodium chloride, sodium sulphate, sodium acetate, zeolite, sodium carbonate, sodium bicarbonate, clay, talc, calcium carbonate, magnesium sulfate, gypsum, calcium sulfate, magnesium oxide, zinc oxide, titanium dioxide, calcium chloride, potassium chloride, magnesium chloride, zinc chloride, saccharides such as sucrose, mono-, di-, and polysaccharides and derivatives such as starch, cellulose, methyl cellulose, ethyl cellulose, propyl cellulose, polyols/sugar alcohols such as sorbitol, maltitol, xylitol, erythritol, and isomalt, PEG, PVP, citric acid or any water soluble solid acid, fatty alcohols or fatty acids and mixtures thereof,
- microcapsules or a microcapsule slurry as defined above, in a powdered form, preferably in an amount comprised between 0.05 to 15 wt%, more preferably between 0.1 and 5 wt% by weight based on the total weight of the composition,
- optionally free perfume oil.

Liquid scent booster

An object of the invention is a consumer product in the form of a liquid scent booster composition comprising:

- an aqueous phase,
- a surfactant system essentially consisting of one or more than one non-ionic surfactant, wherein the surfactant system has a mean HLB between 10 and 14, preferably chosen in the group consisting of ethoxylated aliphatic alcohols, POE/PPG (polyoxyethylene and polyoxypropylene) ethers, mono and polyglyceryl esters, sucrose ester compounds, polyoxyethylene hydroxylesters, alkyl polyglucosides, amine oxides and combinations thereof;
- a linker chosen in the group consisting of alcohols, salts and esters of carboxylic acids, salts and esters of hydroxyl carboxylic acids, fatty acids, fatty acid salts, glycerol fatty acids, surfactant having an HLB less than 10 and mixtures thereof, and
- microcapsules or a microcapsule slurry as defined above, in the form of a slurry, preferably in an amount comprised between 0.05 to 15 wt%, more preferably between 0.1 and 5 wt% by weight based on the total weight of the composition,
- optionally free perfume oil.

Hair coloration

An object of the invention is a consumer product in the form of an oxidative hair coloring composition comprising:

- an oxidizing phase comprising an oxidizing agent and an alkaline phase comprising an alkakine agent, a dye precursor and a coupling compound; wherein said dye precursor and said coupling compound form an oxidative hair dye in the presence of the oxidizing agent, preferably in an amount comprised between 85 and 99.95% by weight based on the total weight of the composition,
- microcapsules or a microcapsule slurry as defined above, preferably in an amount comprised between 0.05 to 15 wt%, more preferably between 0.1 and 5 wt% by weight based on the total weight of the composition,
- optionally free perfume oil.

Perfuming composition

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

- 0.1 to 30%, preferably 0.1 to 20% of microcapsules or a microcapsule slurry as defined previously,
- 0 to 40%, preferably 3-40% of perfume, and

- 20-90%, preferably 40-90% of ethanol, by weight based on the total weight of the perfuming composition.

FURTHER APPLICATIONS

The core-shell microcapsules disclosed herein may be part of a mulch film.

As used herein, the term 'mulch film' refers to a thin polymeric or composite sheet applied to the soil surface to protect crops by regulating soil temperature, retaining moisture, suppressing weed growth, and reducing erosion. Mulch films may be composed of synthetic or biodegradable materials and are typically designed for temporary use during a crop cycle, often requiring collection and disposal after use. A further advantage of the present invention is that the biodegradable core-shell microcapsules incorporated within the mulch film provide an environmentally friendly solution, as they can naturally degrade in the soil, reducing long-term environmental impact and minimizing residue accumulation.

In other words, the core-shell microcapsules disclosed herein may also be used as a component in a mulch film, preferably in a biodegradable mulch film.

In particular, the core-shell microcapsules disclosed herein may be used as a mulch film.

The shell of the core-shell microcapsules disclosed herein may be used as a fertilizer. Phosphorus is an essential macronutrient for plant growth, playing a crucial role in energy transfer, root development, and overall crop yield. When incorporated into the microcapsule shell, phosphorus can gradually release into the soil as the shell degrades, ensuring sustained nutrient availability to plants. This controlled release mechanism enhances phosphorus uptake efficiency, minimizing leaching losses and environmental runoff, which are common concerns with conventional phosphorus fertilizers.

The core-shell microcapsule disclosed herein may also be used as a delivery system for additional fertilizing 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 phosphorous compounds

Preparation of tris(4-formylphenyl) phosphate (1): In a 100 ml flask under N_2, 4-hydroxybenzaldehyde (12.24g, 100.23mmol), triethylamine (15 mL, 107.62mmol) were added in THF (40mL). Temperature was cooled to 5°C. A solution of phosphorus oxychloride (3 mL, 31.87mmol) in THF (40 mL) was added dropwise and the reaction mixture was stirred to room temperature over night. A white solid precipitated. The solid was filtered and the solvent was distilled off. The crude product was dissolved with ethyl acetate (150 mL) and washed three times with 100 mL of water, and once with brine (100 mL). Organic layer was dried with $MgSO_4$, filtered and the solvent was distilled off. The solid was recrystallized in ethyl acetate/heptane mixture.

NMR δ_P ($CDCl_3$, ppm): -19.71; δ_C ($CDCl_3$, ppm): 190.41, 154.30, 134.20, 131.89, 120.69.

Preparation of tris(4-formyl-2-methoxyphenyl) phosphate (2): : In a 100 mL flask under N_2, 4-hydroxy-3-methoxy-benzaldehyde (7.52 g, 49.44 mmol), triethylamine (7.5 mL, 107.62 mmol) were added in THF (40 mL). A solution of phosphorus oxychloride (1.5 mL, 31.87 mmol) in THF (20 mL) was added dropwise and the reaction mixture was stirred to 60°C for 15 h. A white solid precipitated, it was filtered off and the solvent was distilled off. The solid was recrystallized in ethyl acetate/heptane (6/4) at 90°C.

NMR δ_P ($(CD_3)_2CO$, ppm): -18.27; δ_C ($(CD_3)_2CO$, ppm): 191.68, 152.29, 144.99, 136.03, 124.49, 122.56, 112.84, 56.62.

Preparation of triallyl 3,3',3''-((oxo-λ^5-phosphanetriyl)tris(oxy))tribenzoate (3): A solution of allyl 3-hydroxybenzoate (9.18 g, 51.5 mmol) and triethylamine (21.76 mL, 156.12 mmol) in anhydrous toluene (90 mL) was slowly added dropwise into a solution of phosphorus oxychloride (1.6 mL, 17.17 mmol) in toluene (10 mL) at 0°C under vigorous stirring. Then, the reaction mixture was stirred at room temperature for 3 h. A solution of NaOH (3.0 g) in water (10 mL) was added to the reaction mixture. The organic layer was separated and the aqueous layer was backextracted with toluene (5 x 50 mL). The combined organic layers were washed with saturated brine (3 x30 mL) and dried over $MgSO_4$. The solvent was distilled off to afford 7.71 g of a colorless liquid (yield = 78%).

NMR δ_C ($CDCl_3$, ppm): 164.91, 150.21, 132.31, 131.88, 130.10, 127.14, 124.69, 121.31, 118.64, 65.96.

Preparation of tris(3-chlorocarbonylphenyl) phosphate (4): This preparation was carried out in two steps. First, allyl 3-bis(3-allyloxycarbonylphenoxy)phosphoryloxybenzoate (NICP2576, 3.74 g,

6.46 mmol) and phenylsilane (5.02 mL, 39.07 mmol) were dissolved in dry THF (130 mL) under nitrogen. Tetrakis(triphenylphosphine)palladium (0.42 g, 0.36 mmol) was then added and the mixture was stirred for 60 h at room temperature to afford a gel. The solvent was distilled off and the solid was washed three times with ethyl acetate (150 mL) to afford 2.63 g of 3-bis(3-carboxyphenoxy)phosphoryloxybenzoic acid. Secondly, 3-bis(3-carboxyphenoxy)phosphoryloxybenzoic acid (0.7 g, 1.53 mmol) in thionyl chloride (5.0 mL, 68.55 mmol) were added under nitrogen to give a solution. Dimethylformamide over molecular sieve (0.06 g, 0.8 mmol) was added and the reaction mixture was stirred at 75°C for 3 h, the temperature was cooled down to room temperature and stirred for 15 h. Thionyl chloride was distilled off and the product was dried under vacuum to afford an oil.

NMR δ_P (DMSO-d6, ppm): -17.00; δ_C (DMSO-d6, ppm): 165.88, 149.65, 132.92, 130.82, 126.98, 124.44, 120.35.

Preparation of tris(3-formylphenyl) phosphate (5): In a 100 ml flask under N_2, 3-hydroxybenzaldehyde (51.88 g, 424.80 mmol), triethylamine (200 mL, 1.43 mol) were added in ethyl acetate (160 mL). The temperature was cooled to 5°C. A solution of phosphorus oxychloride (10 mL,106.20 mmol) in ethyl acetate (110 mL) was added dropwise and the reaction mixture was stirred to room temperature over night. A white solid precipitated. The solid was filtered and the solvent was distilled off. The crude product was dissolved with ethyl acetate (500 mL) and washed with an aqueous solution of ammonium chloride at 10% (50 mL), water (50 mL), and brine (50 mL). Organic layer was dried with $MgSO_4$, filtered and the solvent was distilled off to afford a pure solid with very good yield (95%).

NMR δ_P ($CDCl_3$, ppm): -17.90; δ_C ($CDCl_3$, ppm): 190.73, 150.68, 138.15, 130.94, 127.67, 126.05, 120.32.

Preparation of tris(3-hydroxypropyl) phosphate (6): In a 100 ml three-necked round bottom flask equipped with a condenser and a temperature probe under N_2, 3-hydroxypropylacetate (origin: dsm-firmenich, Switzerland, 15.21 g, 128.76 mmol) was dissolved in THF (40 mL). A solution of phosphorus oxychloride (4 mL, 42.92 mmol) in THF (24 mL) was added dropwise while the temperature was monitored to remain below 5°C. The reaction was stirred up to room temperature for 24 h. A white solid precipitated. The solid was filtered and the solvent was distilled off to afford a colorless oil, which was purified by liquid chromatography (silica, ethyl acetate:*n*-heptane = 8:2, m = 8.60 g).

NMR δ_P ($CDCl_3$, ppm): 0.58; δ_C ($CDCl_3$, ppm):64.85, 57.99, 32.87.

3-[Bis(3-acetoxypropoxy)phosphoryloxy]propyl acetate (7, 2.01 g, 5.05 mmol) was dissolved in a suspension of anhydrous potassium carbonate (0.48 g, 3.46 mmol) in anhydrous methanol (20 mL).

The reaction mixture was stirred at room temperature for 4 h. Then, the pH of the mixture was set to 7 by using a solution of HCl in methanol at 1%. The solvent mixture was distilled off and the product was extracted three times with 5 mL of a mixture of acetone:methanol 10:1, and filtered at 0.45 µm. The solvent mixture was distilled off and the product was dried under vacuum to afford a colorless oil. The structure was confirmed by 31P NMR. The product was used without further purification.
NMR δ_P ($CDCl_3$, ppm): -0.92; δ_C ($CDCl_3$, ppm): 170.91, 64.41, 60.38, 29.55, 20.88.

Preparation of tris(2-ethoxy-4-formyl-phenyl) phosphate (8): The product was prepared according to the protocol used with tris(4-formylphenyl) phosphate (**1**) to afford a white solid.

Preparation of tris(2,2-dimethyl-3-oxo-propyl) phosphate (9): In a 100 ml three-necked round bottom flask equipped with a condenser and a temperature probe under N_2, 3-Hydroxy-2,2-dimethylpropanal (10.17 g, 96.56 mmol) was dissolved in THF (40 mL). A solution of phosphorus oxychloride (3 mL, 32.19 mmol) in THF (10 mL) was added dropwise at a temperature below 5°C. The reaction mixture was stirred up to room temperature for 24 h. A white solid precipitated. The solid was filtered and the solvent was distilled off to afford a solid, which was washed with *n*-heptane to afford the compound.
NMR δ_P ($CDCl_3$, ppm): -13.60 (large peak).

Preparation of tris(3-oxopropyl) phosphate (10): In a 100 ml flask under N_2, 3,3-diethoxypropan-1-ol (5.23 mL, 32.19 mmol) and pyridine (2.86 mL, 35.41 mmol) were dissolved in THF (16 mL) and the temperature was cooled at 5°C. Then a solution of phosphorus oxychloride (1 mL, 10.73 mmol) in THF (11 mL) was added dropwise at 5°C. The reaction mixture was stirred overnight. A white solide precipitated. It was filtered and the solvent was distilled off. The tris(3,3-diethoxypropyl) phosphate (**11**) was purified by liquid chromatography with a mixture of ethyl acetate:*n*-heptane 5:5.
NMR δ_P ($CDCl_3$, ppm): -0.99; δ_C ($CDCl_3$, ppm): 99.79, 64.29, 61.82, 34.83, 15.33.
In a 25 ml three necked round bottom flask, tris(3,3-diethoxypropyl) phosphate (0.5 g, 1.02 mmol) was dissolved in THF (10 mL). A solution of HCl in dioxane (2 M, 0.84 mL) was added and the reaction mixture was stirred for 15 h. The solvent was distilled off to afford **10**.
NMR δ_P ($CDCl_3$, ppm): -0.43; δ_C ($CDCl_3$, ppm): 195.45, 66.30, 55.97, 30.61.

Preparation of tris(2-vinyloxyethyl) phosphate (12): In a 100 ml flask under N_2, ethylene glycol monovinyl eher (2.95 mL, 32.19 mmol) and pyridine (2.86 mL, 35.41 mmol) were dissolved in THF (16 mL) at 5°C. Then a solution of phosphorus oxychloride (1 mL, 10.73 mmol) in THF (11 mL) was added dropwise at a temperature of 5°C. The reaction mixture was stirred overnight. A white solide precipitated. It was filtered and solvent was distilled off. The compound was purified by liquid chromatography with a mixture of ethyl acetate:*n*-heptane 5:5 to afford 1.2 g of a colorless oil.

NMR δ_P ($CDCl_3$, ppm): -1.20; δ_C ($CDCl_3$, ppm): 151.32, 87.24, 66.59, 65.96.

Preparation of tris[(2-oxo-1,3-dioxolan-4-yl)methyl] phosphate (13): In a 100 ml three-necked round bottom flask equipped with a condenser and a temperature probe under N_2, glycerol-1,2-carbonate (1.66 mL, 17.69 mmol) and pyridine (1.75 mL, 21.64 mmol) were dissolved in THF (40 mL). A solution of phosphorus oxychloride (0.61 mL, 6.52 mmol) in THF (10 mL) was added dropwise at 5°C. After 2 h, acetonitrile was added (20 mL) to give a solution. The reaction was warmed up to room temperature and stirred overnight. The solvent mixture was distilled off and the crude was dissolved in acetone. A solid precipitated and was filtered. Solvent was distilled off and the product was washed with ethyl acetate and dried to afford a mixture of tris[(2-oxo-1,3-dioxolan-4-yl)methyl] phosphate and bis[(2-oxo-1,3-dioxolan-4-yl)methyl] phosphate (**14**).
NMR δ_P ($CDCl_3$, ppm): -1.39.

Preparation of ethyl bis(4-formyl-2-methoxy-phenyl) phosphate (15): In a 100 ml flask under N_2, 4-hydroxy-3-methoxy-benzaldehyde (7.46g, 49.04mmol) and triethylamine (7.7 mL, 55.21 mmol) were dissolved in THF (25 mL) Temperature was cooled at 5°C. Then a solution of ethyl phosphorodichloridate (2 mL, 16.35 mmol) in THF (17 mL) was added dropwise at 5°C. The reaction mixture was stirred overnight. A white solid precipitated. It was filtered and THF was distilled off. Crude product was dissolved with ethyl acetate (77 mL) and washed with 100 mL of NH_4Cl 10% solution in water, 100 mL of water, 100 mL of brine. Organic layer was dried with $MgSO_4$, filtered and evaporated. An yellow oil was obtained and was purified by liquid chromatography in ethyl acetate/ *n*-heptane 3/7.
NMR δ_P ($CDCl_3$, ppm): -12.63; δ_C ($CDCl_3$, ppm): 190.85, 151.42, 144.60, 134.36, 124.86, 121.58, 110.99, 66.25, 56.13, 16.03.

Preparation of tris(5-formyl-2-methoxy-phenyl) phosphate (16): the product was prepared with 10 g of 3-hydroxy-4-methoxy-benzaldehyde (isovanillin, 63.73 mmol) according to the protocol used to prepare tris(3-formylphenyl) phosphate (**5**).

Preparation of tris[(5-formyl-2-furyl)methyl] phosphate (17): In a 100 mL flask under N_2, 5-hydroxymethyl-2-furaldehyde (4.33 g, 34.33 mmol) and triethylamine (5.2 mL, 37.55 mmol) were dissolved in THF (30 mL) at 5°C. Then a solution of phosphorus oxychloride (1 mL, 10.73 mmol) in THF (20 mL) was added dropwise at 5°C. The reaction mixture was stirred overnight. A white solid precipitated. It was filtered and solvent was distilled off. Crude product was dissolved with ethyl acetate (250 mL) and washed with 100 mL of water (three times) and 100 mL of brine. Organic layer was dried with $MgSO_4$, filtered and evaporated. Product was recrystallized in ethyl acetate/heptane mixture.

NMR δ_P ($CDCl_3$, ppm): -0.79.

Preparation of tris(5-oxopentyl) phosphate (18): In a 100 mL flask equipped with a condenser under N_2, phosphorus oxychloride (1 mL, 10.73 mmol) and pyridine (2.86 mL, 35.41 mmol) were dissolved in THF (40 mL). A solution of 5-hydroxypentanal (3.62 g, 35.41 mmol) in THF (20 mL) was added dropwise at 5°C. The reaction mixture was stirred at room temperature for 24 h. A white solid precipitated. It was filtered and THF was distilled off. Crude product was purified by liquid chromatography.

NMR δ_P ($CDCl_3$, ppm): 0.57; δ_C ($CDCl_3$, ppm): 201.91, 63.92, 32.05, 25.27, 20.41.

Preparation of 4-dichlorophosphoryloxybenzaldehyde (19): Phosphorus oxychloride (5 mL, 53.11 mmol) and triethylamine (8.8 mL, 63.14 mmol) were disolved in THF (40 mL) at 0°C. A solution of 4-hydroxybenzaldehyde (3.21 g, 26.27 mmol) in THF (40 mL) was added dropwise at 0°C. The reaction mixture was filtered and the product was obtained after evaporation of the solvent. Product was used without further purification.

Preparation of ethyl bis(3-formylphenyl) phosphate (20): the product was prepared according to the protocol used to prepare ethyl bis(4-formyl-2-methoxy-phenyl) phosphate (**15**) with 9.25 g of 3-hydroxybenzaldehyde.

NMR δ_P ($CDCl_3$, ppm): -12.11; δ_C ($CDCl_3$, ppm): 190.88, 151.07, 138.11, 130.70, 127.04, 126.11, 102.46, 66.23, 16.13.

Preparation of ethyl bis(4-formylphenyl) phosphate (21): the product was prepared according to the protocol used to prepare ethyl bis(4-formyl-2-methoxy-phenyl) phosphate (15) with 9.24 g of 4-hydroxybenzaldehyde.

NMR δ_P ($CDCl_3$, ppm): -13.30; δ_C ($CDCl_3$, ppm): 190.59, 154.85, 133.75, 131.77, 120.64, 66.41, 16.11.

Preparation of tris[4-(2,5-dioxopyrrol-1-yl)phenyl] phosphate (22): the product was prepared with 3 g of 1-(4-Hydroxyphenyl)-1H-pyrrole-2,5-dione (16 mmol) according to the protocol used to prepare tris(3-formylphenyl) phosphate (**5**).

NMR δ_P ($CDCl_3$, ppm): -17.26; δ_C ($CDCl_3$, ppm): 170.25, 149.17, 135.22, 129.79, 129.15, 121.04.

Preparation of tris[2-formylphenyl] phosphate (23): the product was prepared with 5.2 mL of 2-hydroxybenzaldehyde (49 mmol) according to the protocol used to prepare tris(3-formylphenyl) phosphate (**5**).

NMR δ_P ($CDCl_3$, ppm): -18.90.

Preparation of sodium bis(3-formylphenyl) phosphate (24): sodium iodide (0.45 g, 3.01 mmol) was added to a solution of **20** (1.00 g, 2.99 mmol) in Acetone (10 mL) at room temperature. The reaction mixture was stirred for 40 h at room temperature. The precipitate was collected by suction filtration, washed with acetone and dried in vacuum to obtain a white solid.

NMR δ_P (DMSO-d6, ppm): -11.99; δ_C (DMSO-d6, ppm): 192.78, 150.90, 138.38, 131.74, 127.63, 126.55, 120.24.

Preparation of tris[4-aminophenyl] phosphate (25): In a 100 ml flask under N_2, tert-butyl (4-hydroxyphenyl)carbamate (6.94 g, 32.19 mmol), triethylamine (4.93 mL, 35.41 mmol) were added in THF (20 mL). The temperature was cooled to 5°C. A solution of phosphorus oxychloride (1 mL,10.73 mmol) in THF (20 mL) was added dropwise and the reaction mixture was stirred to room temperature overnight. A white solid precipitated. The solid was filtered and the solvent was distilled off. The crude product was dissolved with ethyl acetate (50 mL) and washed with an aqueous solution of ammonium chloride at 10% (20 mL), water (20 mL), and brine (20 mL). Organic layer was dried with $MgSO_4$, filtered and the solvent was distilled off to afford a pure tert-butyl-N-[4-bis[4-(tert-butoxycarbonylamino)phenoxy] phosphoryloxyphenyl]carbamate (**26**) with very good yield (95%).

NMR δ_C ($CDCl_3$, ppm): 152.78, 145.64, 135.99, 120.54, 119.78, 80.69, 28.32.

Phosphate triester 26 (0.3 g) was dissolved in a mixture of dichloromethane and trifluoroacetic acid (4:1, v:v) (12 mL) at room temperature for 24 h. The solvents were distilled off. The resulting solid was dissolved in ethyl acetate (25 mL) and washed with water (25 mL) and brine (25 mL). The organic phase was dried over sodium sulfate and the solvent was distilled off to afford the product.

Preparation of 4-bis(4-formylphenoxy)phosphinothioyloxybenzaldehyde (27): In a 100 ml flask under N_2, 4-hydroxybenzaldehyde (8.84 g, 72.36 mmol), triethylamine (11.36 mL, 81.48 mmol) were added in ethyl acetate (106 mL). The temperature was cooled to 5°C. A solution of phosphorus oxychloride (2.50 mL,24.13 mmol) in ethyl acetate (15 mL) was added dropwise and the reaction mixture was stirred to room temperature overnight. A white solid precipitated. The solid was filtered and the solvent was distilled off. The crude product was dissolved with ethyl acetate (50 mL) and washed with an aqueous solution of ammonium chloride at 10% (2 x 200 mL), and brine (200 mL). Organic layer was dried with $MgSO_4$, filtered and the solvent was distilled off to afford a pure solid.

NMR δ_C (DMSO-d6, ppm): 191.81, 153.84, 134.09, 131.76, 121.71.

Preparation of tris[4-(5-hydroxy-1,3-dioxan-2-yl)phenyl] phosphate (28): In a 100 ml flask under N_2, tris(4-formylphenyl) phosphate (5.0 g, 72.36 mmol), toluene-4-sulfonic acid monohydrate (0.12 g, 0.61 mmol) were added in glycerol (6.73 g, 73.11 mmol) and toluene (35 mL). The reaction mixture was stirred at 75°C overnight. The solvent was distilled off and the crude product was dissolved with ethyl acetate (50 mL) and washed with water (2 x 100 mL), and brine (50 mL). Organic layer was dried with $MgSO_4$, filtered and the solvent was distilled off to afford an orange oil.

NMR δ_P (DMSO-d6, ppm): -17.59.

Preparation of tris(4-formyl-2-methyl-phenyl) phosphate (29): In a 100 ml flask under N_2, 4-Hydroxy-3-methylbenzaldehyde (5.2 g, 38.19 mmol), triethylamine (6.0 mL, 43.05 mmol) were added in ethyl acetate (20 mL). The temperature was cooled to 5°C. A solution of phosphorus oxychloride (1.2 mL,12.75 mmol) in ethyl acetate (12 mL) was added dropwise and the reaction mixture was stirred to room temperature overnight. A white solid precipitated. The solid was filtered and the organic phase was washed with an aqueous solution of ammonium chloride at 10% (100 mL), water (100 mL),and brine (50 mL). Organic layer was dried with $MgSO_4$, filtered and the solvent was distilled off. The product was purified by liquid chromatography (ethylacetate/heptane 5:5, v:v).

NMR δ_P (DMSO-d6, ppm): -18.78; δ_C (DMSO-d6, ppm): 190.81, 153.10, 134.04, 132.92, 130.54, 129.47, 120.36, 16.25.

Example 2

Preparation of microcapsules according to the invention

General protocol for preparing microcapsules A: 0.71 g of gum Arabic and 0.43 g of carboxymethyl cellulose were dissolved with 0.43 g of phloroglucinol (PHG) in 35.71 g of water. The temperature was maintained at 60°C for 10 minutes. After 10 minutes, a solution of 22.86 g perfume oil (see Table 1) with 1.95 g tris(4-formylphenyl) phosphate (PTE) was warmed up at 60°C for 5 minutes and added to the aqueous solution. The emulsion was prepared with UT at 17,000 rpm for 2 minutes (pH = 5.42), and stirred at 250 rpm with mechanical stirring in reactor or shake at 300 rpm in incubator. The dispersion was cured at 80°C during 4h. A solution of gum Arabic (5.00 g) in water (14.29 g) was added to the composition (pH = 3.64). After 30 minutes, the mixture was cooled down from 80°C to 20°C. After 30 minutes, a solution of chitosan (source: Kitozyme, Belgium, 1.29 g) in 0.3 M HCl (17.86 g) was added over 30 minutes. The dispersion was cured at 60°C over the period of 1 h. To avoid agglomeration, a solution of gum Arabic (0.71 g) in water

(2.14 g) was added to the composition. After 150 minutes at 60°C, the composition was cooled to room temperature to afford the final dispersion (pH = 3.64).

Table 1: Perfume oil composition (also referred to Perfume A)

Ingredient	**% in oil**
Ethyl 2-methyl-pentanoate	3.20%
Eucalyptol	7.80%
2,4-Dimethyl-3-cyclohexene-1-carbaldehyde	0.75%
Aldehyde C_{10}	0.75%
Citronellyl Nitrile	4.30%
Isobornyl acetate	3.00%
2-tert-butyl-1-cyclohexyl acetate	9.80%
Citronellyl Acetate	1.30%
2-Methylundecanal	3.00%
Diphenyloxide	0.80%
Aldehyde C_{12}	1.30%
Dicyclopentadiene acetate	9.85%
Ionone beta	3.30%
Undecalactone gamma	18.75%
Hexyl Salicylate	15.9%
Benzyl Salicylate	16.2%

Example 3

Preparation of microcapsules according to the invention

Capsules were prepared according to the protocol of Example 2 and using tris(3-formylphenyl) phosphate.

Example 4

Stability and biodegradability of microcapsules according to the invention

Retention of microcapsules: General protocol: an aliquot of capsule dispersion (about 10 mg) was introduced in an aluminium pan (see Ouali *et al.*, Polymers for Advanced Technologies (2006), 17(1), 45-52). The mass loss of the sample was measured as a function of time at 50°C in thermogravimeter (Mettler Toledo). The sample was warmed from

25°C to 50°C at 5°C.min^{-1} and then kept at 50°C for 250 minutes. The percentage per minute of mass loss based on the total weight of the sample was estimated as the difference of % measured after 50 (equation 1) and 250 minutes (equation 2), respectively, according to the equation (3). Results were reported in the table below.

$$\%m_{50} = 100 * \frac{m_{50min}}{m_{total}} \quad (1)$$

$$\%m_{250} = 100 * \frac{m_{250min}}{m_{total}} \quad (2)$$

$$-\frac{dm_{\%}}{dt} = -\frac{\%m_{250} - \%m_{50}}{200} \quad (3)$$

Table 2: Samples and results for retention

Sample	$-\frac{dm_{\%}}{dt}$ $(\%/min)$
Microcapsules according to Example 2	0.025
Microcapsules according to Example 3	0.002
Free oil	> 0.040

It can be seen from the above, that the microcapsules of Examples 2 and 3 (according to the invention) have the capacity to retain fragrance oil at 50°C compared to free oil.

Biodegradability of microcapsules: Microcapsule shells were purified from slurries according to the protocol published by Gasparini et al. Resulting polymers were submitted to OECD 301F testing conditions and results are listed in the Table below.

Table 3: Samples and results of biodegradability

Sample	28 days (%)	60 days (%)
Microcapsules according to Example 2	57	63
Microcapsules according to Example 3	64	73

Results showed that the copolymers of the shells are biodegradable with a yield above 60% after 60 days.

Example 5

Preparation of microcapsules according to the invention

Capsules were prepared according to the protocol of Example 2 at pH 3.2 and using different parameters listed in Table 4.

Table 4: Formulations with different process parameters and results of retention and biodegradability

Sample	% Gum Acacia	% CMC	% PHG	% PTE	% Perfume	% Chitosan (20 °C)	Retention (%/min)
A-5	6.24	0.42	0.42	1.90	22.22	1.25	0.006
B-5	6.24	0.42	0.42	1.90	22.22	1.25 (60°C)	0.012
C-5	6.24	0.42	0.42	1.90	22.22	1.25 (10°C)	0.005
D-5	6.21	0.42	0.52	1.88	22.09	1.25	0.002
E-5	6.21	0.42	0.63	1.88	22.07	1.25	0.002
F-5	6.18	0.41	0.72	1.88	22.04	1.24	0.009
G-5	6.16	0.41	1.24	1.87	21.93	1.24	0.003
H-5	6.18	0.41	0.63 in water 0.10 in oil	1.88	22.04	1.24	0.005
I-5	6.24	0.42	0.42	1.42	22.22	1.25	0.006
J-5	6.24	0.42	0.42	0.96	22.22	1.25	0.008

It can be seen from the above, that the microcapsules of Example 5 (according to the invention) have the capacity to retain fragrance oil at 50°C compared to free oil. The biodegradation of microcapsules A-5, B-5, C-5 and E-5 was tested, and a yield greater than 60% after 60 days was obtained for these microcapsules.

Example 6

Preparation of microcapsules according to the invention

Capsules were prepared according to the protocol of Example 2 at pH 3.2 and different anionic polymers in Table 5.

Table 5: Anionic polymers used at 0.42% in formulations and results of retention and biodegradability

Sample	% Gum Acacia	Anionic polymer (0.42%)	Retention (%/min)
A-6	6.24	CMC Decare	0.005
B-6	6.24	Blanose 7LF	0.009
C-6	6.24	Carbocel F MM1	0.014
D-6	6.24	Finnfix 10G	0.020
E-6	6.24	Cekol 30	0.015
F-6	6.24	Carbocel MB5 LB	0.015
G-6	6.24	Hi-Cap	0.020
H-6	6.65	Gum Acacia	0.020
I-6	6.24	Pectin 104APA	0.006
J-6	6.24	LMC pectin	0.007
K-6	6.17	Na Alginate	0.004
L-6	6.24	Carrageenan	0.017
M-6	6.24	PVOH KL506	0.019
N-6	6.22	Sodium polyaspartate	0.005

It can be seen from the above, that the microcapsules of Example 6 (according to the invention) have the capacity to retain fragrance oil at 50°C compared to free oil. The biodegradation of microcapsules B-6, E-6 and N-6 was tested, and a yield greater than 60% after 60 days was obtained for these microcapsules.

Example 7

Preparation of microcapsules according to the invention

Capsules were prepared according to the protocol of Example 2 at pH 3.2 and different cationic polymers in Table 6.

Table 6: Cationic polymers in formulation and results of retention

Sample	Cationic polymer	Retention (%/min)
A-7	Lupin protein 1.25%	0.010
B-7	Solanic 200 1.25%	0.006

It can be seen from the above, that the microcapsules of Example 7 (according to the invention) have the capacity to retain fragrance oil at 50°C compared to free oil.

Example 8

Preparation of microcapsules according to the invention

Capsules were prepared according to the protocol of Example 2 at pH 3.2 with different multifunctional aldehydes in Table 7.

Table 7: Multifunctional aldehydes of the invention in formulations and results of retention

Sample	Phosphate ester monomer (%)	Retention (%/min)
A-8	Monomer (21) 2.29%	0.022
B-8	Monomer (20) 2.29%	0.004
C-8	Monomer (5) 1.51% + Monomer (1) 0.38%	0.006
D-8	Monomer (5) 1.13% + Monomer (1) 0.75%	0.009
E-8	Monomer (27) 1.88%	0.022
F-8	Monomer (29) 1.88%	0.019

It can be seen from the above, that the microcapsules of Example 8 (according to the invention) have the capacity to retain fragrance oil at 50°C compared to free oil.

Example 9

Preparation of microcapsules according to the invention

Capsules were prepared according to the protocol of Example 2 at pH 3.2 with different quantities of gum Acacia and chitosan in Table 8. No third gum Acacia addition was carried out.

Table 8: Multifunctional aldehydes of the invention in formulations and results of retention

Sample	% Gum Acacia	% CMC	% PHG	% PTE	% Perfume	% Chitosan (20 °C)	Retention (%/min)
A-9	5.65	0.52	0.74	1.93	22.7	1.28	0.009
B-9	5.88	0.54	0.77	2.01	23.5	1.06	0.007
C-9	6.12	0.56	0.80	2.09	24.5	0.83	0.005
D-9	5.36	0.54	0.77	2.01	23.6	1.19	0.006
E-9	5.05	0.56	0.80	2.09	24.5	1.10	0.007
F-9	5.26	0.53	0.76	1.97	23.1	1.30	0.007
G-9	4.85	0.54	0.77	2.01	23.6	1.33	0.007
H-9	3.98	0.56	0.80	2.09	24.5	1.38	0.006
I-9	5.66	0.52	0.68	1.75	22.7	1.28	0.010
J-9	5.69	0.52	0.60	1.55	22.8	1.28	0.008
K-9	5.65	0.51	0.73	1.90	22.2	1.38	0.005
L-9	5.93	0.50	0.72	1.86	21.8	1.36	0.007

Example 10

Preparation of microcapsules according to the invention

Protocol for preparing microcapsules A-10: 0.71 g of gum Arabic and 0.52 g of carboxymethyl cellulose were dissolved with 0.75 g of phloroglucinol in 35.71 g of water. The temperature was maintained at 60°C for 10 minutes. After 10 minutes, a solution of 22.86 g perfume oil (see Table 1) with 1.95 g tris(4-formylphenyl) phosphate was warmed up at 60°C for 5 minutes and added to the aqueous solution. The emulsion was prepared with UT at 17,000 rpm for 2 minutes (pH = 5.14). Formic acid was added to adjust pH value to 3.11 and the emulsion was stirred at 250 rpm with mechanical stirring in reactor. The dispersion was cured at 80°C during 4h. The mixture was cooled down from 80°C to 20°C over 30 minutes. A solution of chitosan (source: Kitozyme, Belgium, 1.29 g) in 0.3 M HCl (17.86 g) was added. After 30 minutes, a solution of gum Arabic (5.00 g) in water (14.29 g) was added to the composition. The dispersion was cured at 60°C over the period of 1 h. To avoid agglomeration, a solution of gum Arabic (0.71 g) in water (2.14 g) was added to the composition. After two hours at 60°C, the composition was cooled to room temperature to afford the final dispersion.

Table 9: Multifunctional aldehydes of the invention in formulations and results of retention

Sample	% Gum Acacia	% CMC	% PHG	% PTE	% Perfume	% Chitosan (20 °C)	Retention (%/min)
A-10	6.21	0.50	0.72	1.88	22.1	1.25	0.011

Example 11

Preparation of microcapsules according to the invention

General protocol for preparing microcapsules of Example 11: 0.71 g of gum Arabic and 0.52 g of carboxymethyl cellulose were dissolved with 0.75 g of phloroglucinol in 35.71 g of water. The temperature was maintained at 60°C for 10 minutes. After 10 minutes, a solution of 22.86 g perfume oil (see Table 1) with 1.95 g tris(4-formylphenyl) phosphate was warmed up at 60°C for 5 minutes and added to the aqueous solution. The emulsion was prepared with UT at 17,000 rpm for 2 minutes (pH = 5.07). Formic acid was added to adjust pH value to 3.12 and the emulsion was stirred at 250 rpm with mechanical stirring in reactor. The dispersion was cured at 80°C during 4h. The mixture was cooled down from 80°C to 20°C over 30 minutes. A solution of chitosan (source: Kitozyme, Belgium, 1.29 g) in 0.3 M HCl (17.86 g) was added over 30 minutes. The dispersion was warmed up to 60°C over 30 minutes and cured for two hours. The composition was cooled to room temperature to afford the final dispersion.

Different quantities of chitosan were used in microcapsules B-11 and C-11 (Table 10).

Table 10: Multifunctional aldehydes of the invention in formulations and results of retention

Sample	% Gum Acacia	% CMC	% PHG	% PTE	% Perfume	% Chitosan (20 °C)	Retention (%/min)

A-11	0.87	0.64	0.92	2.39	28.0	1.58	0.000
B-11	0.91	0.67	0.96	2.51	29.4	1.32	0.000
C-11	0.96	0.70	1.01	2.64	30.9	1.04	0.001

Example 12

Preparation of microcapsules according to the invention.

Microcapsules A-12: Potato protein (0.56 g) was dissolved in DI water (27.44 g) with stirring to give a solution as aqueous phase. Tris(4-isocyanatophenyl) thiophosphate (Desmodur RFE) (0.936 g) was vacuumed for 1 min and dissolved in mixture of neobee (1.2 g) and the perfume composition (Perfume Oil A herein-above;10.6137 g) with stirring to give a solution as oil phase. The prepared two phases were mixed using ULTRA-TURRAX at 13.5k rpm for 2 min to obtain a emulsion. To the prepared emulsion, 5% sugar beet pectin (4.5 g) was added drop wise with stirring. The pH value was adjusted to 4 by diluted NaOH. It was stirred at 90°C for 1 h, then cooled to 40°C, and stirred for 4 h, next, it was stirred at 90°C for 0.5 h. Stable microcapsules were obtained.

Table 11: Composition of microcapsules A-12.

Ingredients	**Effective Amount of Ingredient (% wt)[a)]**	**Function**
Potato protein[1)]	1.3	First Polyelectrolyte
Sugar beet pectin[2)]	0.5	Second Polyelectrolyte
DI water	71.4	Solvent
Perfume Oil A	23.8	Encapsulated oil
Tris(4-isocyanatophenyl) thiophosphate[3)]	0.3	Crosslinker
Neobee[4)]	2.7	Co-solvent

1) Solanic 200, origin: Avebe
2) origin: Schweizer Zucker AG
3) Desmodur RFE, Covestro
4) Neobee M5

Microcapsules B-12: Potato protein (0.56 g) was dissolved in DI water (27.44 g) with stirring to give a solution as aqueous phase. Desmodur RFE (0.936 g) was vacuumed for 1 min and dissolved in mixture of neobee (1.2 g) and Perfume Oil A (10.6137 g) with stirring to give a solution as oil phase.

The prepared two phases were mixed using ULTRA-TURRAX at 13.5k rpm for 2 min to obtain a emulsion. To the prepared emulsion, 5% sugar beet pectin (10 g) was added drop wise with stirring. The pH value was adjusted to 4 by diluted NaOH. It was stirred at 90°C for 1 h, then cooled to 40°C, followed by adding laccase (0.36 g of 1 U/g aqueous solution) and stirred for 4 h, next, it was stirred at 90°C for 0.5 h. Stable microcapsules were obtained.

Table 12: Composition of microcapsules B-12.

Ingredients	Effective Amount of Ingredient (% wt)[a)]	Function
Potato protein[1)]	1.3	First Polyelectrolyte
Sugar beet pectin[2)]	0.5	Second Polyelectrolyte
Laccase[3)]	0.0006	Enzyme
DI water	71.4	Solvent
Perfume Oil A	23.8	Encapsulated oil
Tris(4-isocyanatophenyl) thiophosphate[4)]	0.3	Crosslinker
Neobee[5)]	2.7	Co-solvent

1) Solanic 200, origin: Avebe
2) origin: Schweizer Zucker AG
3) Sigma-Aldrich
4) Desmodur RFE, Covestro
5) Neobee M5

Microcapsules C-12: Potato protein (0.56 g) was dissolved in DI water (27.44 g) with stirring to give a solution as aqueous phase. Desmodur RFE (0.936 g) was vacuumed for 1 min and dissolved in mixture of neobee (1.2 g) and Perfume Oil A (10.6137 g) with stirring to give a solution as oil phase.

The prepared two phases were mixed using ULTRA-TURRAX at 13.5k rpm for 2 min to obtain a emulsion. To the prepared emulsion, 5% Gum Arabic (4.5 g) was added drop wise with stirring.

The pH value was adjusted to 4 by diluted NaOH. It was stirred at 90°C for 1 h, then cooled to 40°C, and stirred for 4 h, next, it was stirred at 90°C for 0.5 h. Stable microcapsules were obtained.

Table 13: Composition of microcapsules C-12.

Ingredients	Effective Amount of Ingredient (% wt)[a)]	Function
Potato protein[1)]	1.3	First Polyelectrolyte
Gum Arabic[2)]	0.5	Second Polyelectrolyte
DI water	71.4	Solvent
Perfume Oil A	23.8	Encapsulated oil
Tris(4-isocyanatophenyl) thiophosphate[3)]	0.3	Crosslinker
Neobee[4)]	2.7	Co-solvent

1) Solanic 200, origin: Avebe
2) origin: dsm-firmenich
3) Desmodur RFE, Covestro
4) Neobee M5

Microcapsules D-12: Potato protein (0.75 g) was dissolved in DI water (23.25 g) with stirring to give a solution as aqueous phase. Desmodur RFE (1.248 g) and neobee (1.6 g) and Perfume Oil A (13.152 g) with stirring to give a solution as oil phase.
The prepared two phases were mixed using ULTRA-TURRAX at 13.5k rpm for 2 min to obtain a emulsion. To the prepared emulsion, 5% Gum Arabic (10 g) was added drop wise with stirring. The pH value was adjusted to 4 by diluted NaOH. It was stirred at 90°C for 1 h, then cooled to 40°C, followed by adding 50% glutaraldehyde (0.75 g) and stirred for 4 h, next, it was stirred at 90°C for 0.5 h. Stable microcapsules were obtained.

Table 14: Composition of microcapsules D-12.

Ingredients	Effective Amount of Ingredient (% wt)[a)]	Function
Potato protein[1)]	1.6	First Polyelectrolyte
Gum Arabic[2)]	0.65	Second Polyelectrolyte

Glutaraldehyde[3)]	0.8	Crosslinker
DI water	64.95	Solvent
Perfume Oil A	28.1	Encapsulated oil
Tris(4-isocyanatophenyl) thiophosphate[4)]	0.4	Crosslinker
Neobee[5)]	3.5	Co-solvent

1) Solanic 200, origin: Avebe
2) origin: dsm-firmenich
3) Sigma-Aldrich
4) Desmodur RFE, Covestro
5) Neobee M5

Microcapsules E-12: In a four stream multi-inlet vortex, 4.0% potato protein aqueous solution (adjusted to pH 4) were injected into two steams and 2% Gum Arabic aqueous solution (adjusted to pH 4) were injected into another two streams. The injection was made using the pump (PHD ULTRA, Harvard) under the speed at 40 mL/min. The obtained suspension was used as aqueous phase.

Desmodur RFE (1.17 g) was vacuumed for 1 min and dissolved in mixture of neobee (1.5 g) and L-Lysine diisocyanate ethyl ester (0.3 g) and Perfume Oil A (12.9424 g) with stirring to give a solution as oil phase.

The prepared two phases were mixed using ULTRA-TURRAX at 13.5k rpm for 2 min to obtain a emulsion. It was stirred at 90°C for 2 h. Stable microcapsules were obtained.

Table 15: Composition of microcapsules E-12.

Ingredients	**Effective Amount of Ingredient (% wt)[a)]**	**Function**
Potato protein[1)]	1.4	Polyelectrolyte
Gum Arabic[2)]	0.7	Polyelectrolyte
DI water	68	Solvent
Perfume Oil A	25.9	Encapsulated oil

L-Lysine diisocyanate ethyl ester[3)]	0.6	Crosslinker
Tris(4-isocyanatophenyl) thiophosphate[4)]	0.4	Crosslinker
Neobee[5)]	3	Co-solvent

1) Solanic 200, origin: Avebe
2) origin: dsm-firmenich
3) Sinopharm Chemical Reagent Co.,Ltd.
4) Desmodur RFE, Covestro
5) Neobee M5

Microcapsules F-12: In a four stream multi-inlet vortex, 4.0% potato protein aqueous solution (adjusted to pH 4) were injected into two steams and 2% Gum Arabic aqueous solution (adjusted to pH 4) were injected into another two streams. The injection was made using the pump (PHD ULTRA, Harvard) under the speed at 40 mL/min. The obtained suspension was used as aqueous phase.

Desmodur RFE (2.34 g) was vacuumed for 1 min and dissolved in mixture of benzyl benzoate (4.5 g) and Perfume Oil A (9.8804 g) with stirring to give a solution as oil phase.

The prepared two phases were mixed using ULTRA-TURRAX at 13.5k rpm for 2 min to obtain a emulsion. It was stirred at 90°C for 2 h. Stable microcapsules were obtained.

Table 16: Composition of microcapsules F-12.

Ingredients	**Effective Amount of Ingredient (% wt)[a)]**	**Function**
Potato protein[1)]	1.4	Polyelectrolyte
Gum Arabic[2)]	0.7	Polyelectrolyte
DI water	68.3	Solvent
Perfume Oil A	19.8	Encapsulated oil
Tris(4-isocyanatophenyl) thiophosphate[3)]	0.7	Crosslinker
Benzyl benzoate[4)]	9.1	Co-solvent

1) Solanic 200, origin: Avebe
2) origin: dsm-firmenich
3) Desmodur RFE, Covestro

4) Sinopharm Chemical Reagent Co.,Ltd.

Microcapsules G-12: Potato protein (0.7 g) was dissolved in DI water (31 g) with stirring to give a solution, lysine ethyl ester dihydrochloride (0.7875 g) was added to it, followed by adjusting the pH value to 10 by 30% NaOH, and stirred to give a solution, then a solution with calcium chloride (0.14 g) dissolved in DI water (2.3725 g) was added with stirring to give a suspension as the water phase. Desmodur RFE (2.34 g) was vacuumed for 2 min and dissolved in mixture of benzyl benzoate (4.5 g) and Perfume Oil A (10 g) with stirring to give a solution as oil phase.
The prepared two phases were mixed using ULTRA-TURRAX at 18k rpm for 1 min to obtain an emulsion. The pH value of the obtained emulsion was adjusted to 5 by acetic acid. It was stirred at 90°C for 2 h. Stable microcapsules were obtained.

Table 17: Composition of microcapsules G-12.

Ingredients	Effective Amount of Ingredient (% wt)[a)]	Function
Potato protein[1)]	1.4	Polyelectrolyte
lysine ethyl ester dihydrochloride[2)]	1.6	Nucleophile
Calcium Chloride[3)]	0.3	Complexation agent
DI water	66.7	Solvent
Perfume Oil A	20	Encapsulated oil
Tris(4-isocyanatophenyl) thiophosphate[4)]	0.7	Crosslinker
Benzyl benzoate[5)]	9	Co-solvent

1) Solanic 200, origin: Avebe
2) Sinopharm Chemical Reagent Co.,Ltd.
3) Sinopharm Chemical Reagent Co.,Ltd.
4) Desmodur RFE, Covestro
5) Sinopharm Chemical Reagent Co.,Ltd.

Microcapsules H-12: Potato protein (0.7 g) was dissolved in DI water (31 g) with stirring to give a solution, lysine ethyl ester dihydrochloride (0.7875 g) was added to it, followed by adjusting the pH value to 10 by 30% NaOH, and stirred to give a solution, then a solution with calcium chloride (0.14 g) dissolved in DI water (2.3725 g) was added with stirring to give a suspension as the water

phase. Desmodur RFE (2.34 g) was vacuumed for 2 min and dissolved in mixture of benzyl benzoate (1.5 g) and Perfume Oil A (6.26 g) with stirring to give a solution; PCL-diol (0.75 g) was dissolved in mixture of benzyl benzoate (3 g) and Perfume Oil A (3 g) with stirring at 50°C to give a solution, and it was mixed with the solution containing Desmodur RFE at RT to give a solution as oil phase.

The prepared two phases were mixed using ULTRA-TURRAX at 18k rpm for 1 min to obtain an emulsion. The pH value of the obtained emulsion was adjusted to 5 by acetic acid. It was stirred at 90°C for 2 h. Stable microcapsules were obtained.

Table 18: Composition of microcapsules H-12.

Ingredients	Effective Amount of Ingredient (% wt)[a)]	Function
Potato protein[1)]	1.4	Polyelectrolyte
lysine ethyl ester dihydrochloride[2)]	1.6	Nucleophile
Calcium Chloride[3)]	0.3	Complexation agent
DI water	66.6	Solvent
Perfume Oil A	18.5	Encapsulated oil
Tris(4-isocyanatophenyl) thiophosphate[4)]	0.7	Crosslinker
Benzyl benzoate[5)]	9	Co-solvent
PCL-diol[6)]	1.5	

1) Solanic 200, origin: Avebe
2) Sinopharm Chemical Reagent Co.,Ltd.
3) Sinopharm Chemical Reagent Co.,Ltd.
4) Desmodur RFE, Covestro
5) Sinopharm Chemical Reagent Co.,Ltd.
6) Sigma-Aldrich

Example 13

Performance of microcapsules according to the invention

The storage stability of the capsules in liquid fabric conditioner composition (see Table 19) was evaluated. Microcapsule dispersions (i.e slurry) of the present invention were diluted in the fabric conditioner composition described below to obtain a concentration of encapsulated

perfume of 0.116%. The fabric conditioner was stored at 38°C. The amount of perfume having leaked out of the capsules was then measured by solvent extraction and GC-MS analysis.

Table 19: Liquid fabric conditioner composition:

Product	Wt %
Stepantex VL 90A	8.88
Calcium Chloride Sol. 10%	0.36
Proxel GXL	0.04
Encapsulated perfume	0.116
Water	To 100
TOTAL	100

Microcapsules of Example 3 show a leakage of 12%.

The storage stability of the capsules in Liquid Detergent was evaluated. Microcapsule dispersions (i.e slurry) of the present invention were diluted in the liquid detergent composition (P&G US Tide Free & Gentle HE, ingredients listed below) to obtain a concentration of encapsulated perfume of 0.116%. The detergent was stored at 38°C. The amount of perfume having leaked out of the capsules was then measured by solvent extraction and GC-MS analysis. Leakage results after three days at 38°C are listed below.

Table 20: 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

Microcapsules of Example 3 show a leakage of 17%.

Example 14

Preparation of microcapsules according to the invention

Capsules were prepared according to the protocol of Example 2 and using other phenols (see table below) instead of phloroglucinol.

Table 21: Phenols used in formulations and results of retention

Example	Phenol	$-\frac{dm_{\%}}{dt}$ $(\%/min)$Retention (%/min)
6.1	Resorcinol	Not measured
6.2	Gallic acid	0.036
6.3	Cardanol	0.028
6.4	Propyl gallate	0.026
	Free oil	>0.040

Example 15

Spray-dried microcapsules preparation

Emulsions A-E having the following ingredients are prepared.

Table 22: 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%
Exemplified Microcapsules	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%
Exemplified microcapsules	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) CapsulTM, Ingredion

2) Maltodextrin 10DE origin: Roquette

3) Maltose, Lehmann & Voss

4) Silica, Evonik

5) see table 23

Table 23: 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-naphtalenyl)-1-ethanone, International Flavors & Fragrances, USA

4) Firmenich SA, Switzerland

5) Methyl dihydrojasmonate, Firmenich SA, Switzerland

6) Firmenich SA, Switzerland

Components for the polymeric matrix (Maltodextrin and capsul™, 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 16

Liquid scent booster composition

A sufficient amount of exemplified microcapsules is weighed and mixed in a liquid scent booster to add the equivalent of 0.2% perfume.

Table 24: 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%

1) Deceth-8; trademark and origin : KLK Oleo
2) Laureth-9; ; trademark and origin
3) Plantacare 2000UP; trademark and origin : BASF

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.

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.

Example 17

Liquid detergent composition

A sufficient amount of exemplified microcapsules is weighed and mixed in a liquid detergent to add the equivalent of 0.2% perfume.

Table 25: 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

6) Hostapur SAS 60; Origin: Clariant
7) Edenor K 12-18; Origin: Cognis
8) Genapol LA 070; Origin: Clariant
9) Origin: Genencor International
10) Aculyn 88; Origin: Dow Chemical

Example 18

Unit dose formulation

A sufficient amount of exemplified microcapsules is weighed and mixed in a unit dose formulation to add the equivalent of 0.2% perfume.

The unit dose formulation can be contained in a PVOH (polyvinyl alcohol) film.

Table 26: Unit dose composition

Ingredients	**Concentration [wt%]**
C12 - C14 alkyl poly ethoxylate	15
C12 - C14 alkyl poly ethoxylate sulfate Mono Ethanol Amine salt	9.5
Linear Alkylbenzene sulfonic acid	17
Citric Acid	0.5
C12 - C18 Fatty Acid	17
Enzymes	1.2
Fluorescent brightener	0.3
1,2 propanediol	12
Glycerol	9
Sodium Hydroxide	1
Mono Ethanol Amine	6
PDMS	2.5
Potassium sulphite	0.2
Water	8.8

Total	100

Example 19

Powder detergent composition

A sufficient amount of exemplified microcapsules is weighed and mixed in a powder detergent composition to add the equivalent of 0.2% perfume.

Table 27: Powder detergent composition

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

Concentrated All Purpose Cleaner composition

A sufficient amount of exemplified microcapsules is weighed and mixed in a concentrated all-purpose cleaner composition to add the equivalent of 0.2% perfume.

Table 28: 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

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 21

Solid scent booster composition

The following compositions are prepared.

Table 29: Salt-based solid scent booster compositions

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

Table 30: Urea-based solid scent booster compositions

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

Example 22

Shampoo composition

A sufficient amount of exemplified microcapsules is weighed and mixed in a shampoo composition to add the equivalent of 0.2% perfume.

Table 31: 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 23

Shampoo composition

A sufficient amount of exemplified microcapsules is weighed and mixed in a shampoo composition to add the equivalent of 0.2% perfume.

Table 32: 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
	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 24

Rinse-off hair composition

A sufficient amount of exemplified microcapsules is weighed and mixed in a rinse-off composition to add the equivalent of 0.2% perfume.

Table 33: 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
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

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 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.

Example 25

Antiperspirant spray anhydrous composition

A sufficient amount of exemplified microcapsules is weighed and mixed in an antiperspirant spray anhydrous composition to add the equivalent of 0.2% perfume.

Table 34: 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
3) Bentone® 38; trademark and origin : Elementis Specialities
4) Micro Dry Ultrafine; origin : Reheis

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).

Example 26

Antiperspirant spray emulsion composition

A sufficient amount of exemplified microcapsules is weighed and mixed in antiperspirant spray emulsion composition to add the equivalent of 0.2% perfume.

Table 35: 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

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
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 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

Example 27

Deodorant spray composition

A sufficient amount of exemplified microcapsules is weighed and mixed in antiperspirant deodorant spray composition to add the equivalent of 0.2% perfume.

Table 36: 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

All the ingredients according to the sequence of the Table 36 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 28

Antiperspirant roll-on emulsion composition

A sufficient amount of exemplified microcapsules is weighed and mixed in antiperspirant roll-on emulsion composition to add the equivalent of 0.2% perfume.

Table 37: 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
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 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 29

Antiperspirant roll-on composition

A sufficient amount of exemplified microcapsules is weighed and mixed in antiperspirant roll-on composition to add the equivalent of 0.2% perfume.

Table 38: 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
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

Example 30

Antiperspirant roll-on composition

A sufficient amount of exemplified microcapsules is weighed and mixed in antiperspirant roll-on emulsion composition to add the equivalent of 0.2% perfume.

Table 39: 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

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.

Example 31

Deodorant pump without alcohol formulation

A sufficient amount of exemplified microcapsules is weighed and mixed in the following composition to add the equivalent of 0.2% perfume.

Table 40: 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

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

Example 32

Deodorant pump with alcohol formulation

A sufficient amount of exemplified microcapsules is weighed and mixed in the following composition to add the equivalent of 0.2% perfume.

Table 41: 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

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 33

Talc formulation

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 34

Shower-gel Reference

A sufficient amount of exemplified microcapsules is weighed and mixed in the following composition to add the equivalent of 0.2% perfume.

Table 42: shower gel composition

Ingredients	Amount (% wt)	Function
WATER deionized	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

1) EDETA B POWDER; trademark and origin: BASF
2) CARBOPOL AQUA SF-1 POLYMER; trademark and origin: NOVEON
3) ZETESOL AO 328 U; trademark and origin: ZSCHIMMER & SCHWARZ
4) TEGO-BETAIN F 50; trademark and origin: GOLDSCHMIDT
5) KATHON CG; trademark and origin: ROHM & HASS

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

Example 35

Shower-gel composition

A sufficient amount of exemplified microcapsules is weighed and mixed in the following composition to add the equivalent of 0.2% perfume.

Table 43: 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
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)).

Example 36

Shower-gel composition

A sufficient amount of exemplified microcapsules is weighed and mixed in the following composition to add the equivalent of 0.2% perfume.

Table 44: 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 37

Hand Dishwash

A sufficient amount of exemplified microcapsules is weighed and mixed in the following composition to add the equivalent of 0.2% perfume.

Table 45: Hand dishwash composition

Ingredients	**Amount (% wt)**	**Function**
Linear alkylbenzene sulfonic acid (1)	20	Anionic surfactant
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

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.

Example 38

Toothpaste formulation

A sufficient amount of a microcapsule slurry M (prepared according to the protocol disclosed in example 1 except that a menthol flavor is encapsulated) is weighed and mixed in the following composition to add the equivalent of 0.2% flavor.

Table 46: Toothpaste formulation

Ingredients	**Amount (% wt)**
Polyethylene glycol 400	2.0%
Xanthan Gum	0.6%
Sorbitol 70% Solution	50%
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 39

Dicalcium Phosphate based toothpaste formulation

A sufficient amount of a microcapsule slurry M (prepared according to the protocol disclosed in example 1 except that a menthol flavor is encapsulated) is weighed and mixed in the following composition to add the equivalent of 0.2% flavor.

Table 47: 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%
Silica[1)]	3.0%
TOTAL	100%

1) Aerosil®200; trademark and origin:

Example 40

Mouthwash alcohol free formulation

A sufficient amount of a microcapsule slurry M (prepared according to the protocol disclosed in example 1 except that a menthol flavor is encapsulated) is weighed and mixed in the following composition to add the equivalent of 0.2% flavor.

Table 48: 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 41

Mouthwash formulation

A sufficient amount of a microcapsule slurry M (prepared according to the protocol disclosed in example 1 except that a menthol flavor is encapsulated) is weighed and mixed in the following composition to add the equivalent of 0.2% flavor.

Table 49: Mouthwash formulation

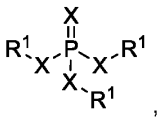
Ingredients	**Amount (% wt)**
Ethyl Alcohol 190 Proof	15.0%
Flavor	0.240%
DI/Purified Water	Q.S to Final Wt.
Poloxamer 407 NF	0.240%
Sodium Lauryl Sulfate	0.040%
Sorbitol 70% Solution	10.0%
Sodium Saccharin	0.030%
Glycerine	3.0%
Sodium Benzoate	0.100%
Sucralose	0.020%
Benzoic Acid	0.050%
TOTAL	100%

CLAIMS

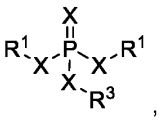
1- A core-shell microcapsule comprising:

- a core comprising a hydrophobic material, preferably comprising a perfume oil, and
- a shell obtainable from a polymerization reaction of at least one phosphorous compound of formula (I) and/or one compound of formula (II), and/or one compound of formula (III) and, preferably a polyfunctional monomer,

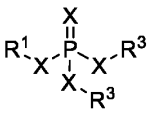
wherein the compound of formula (I) to (III) are as following:



Formula (I)



Formula (II)



Formula (III)

wherein

X, each independently, represents O, S, and/or N-R^2,

R^1, each independently, represents R^4-Y_n with n representing an integer from 1 to 6,

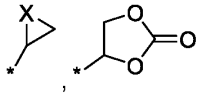
R^2, each independently, represent H or a C_1 to C_{10} hydrocarbon moiety, optionally comprising one or more O, S and/or N atoms,

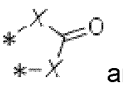
R^3, each independently, represent H, Na^+, K^+, or a C_1 to C_{10} hydrocarbon moiety, optionally comprising one or more O, S and/or N atoms,

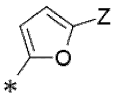
R^4, each independently, represents a C_1 to C_{20} hydrocarbon moiety, optionally comprising one or more O, S and/or N atoms, and

Y, each independently, represents

- -OH, -SH, -NHR^2, -CHO, -NCO,and/or -COCl;
- a strained heterocycle of the following structures:



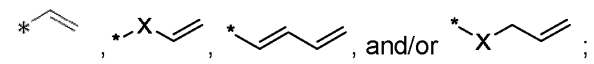
, a 5- or 6- membered ring comprising  and/or



wherein Z is H or –CHO;

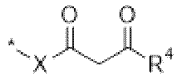
- a free-radical polymerizable function like (meth)acrylates and/or (meth)acrylamides and/or maleimide;

- one of the following olefins:



and/or

- one of the following malonate functions:



2- The core-shell microcapsule according to claim 1, when X-R^1 and/or X-R^2, each independently, comprises a phenol moiety, the pKa of the corresponding monomer H-X-R^1 and/or H-X-R^2, each independently, is between 6 and 11, more preferably between 7 and 10, even more preferably between 7.5 and 9.

3- The core-shell microcapsule according to claim 1 or 2, the compound of formula (I) to (III) is selected from the group consisting of tris(4-formylphenyl) phosphate, tris(4-formyl-2-methoxyphenyl) phosphate, triallyl 3,3',3''-((oxo-λ^5-phosphanetriyl)tris(oxy))tribenzoate, tris(3-chlorocarbonylphenyl) phosphate, tris(3-formylphenyl) phosphate, tris(3-hydroxypropyl) phosphate, tris(2-ethoxy-4-formyl-phenyl) phosphate, tris(2,2-dimethyl-3-oxo-propyl) phosphate, tris(3-oxopropyl) phosphate, tris(2-vinyloxyethyl) phosphate, tris[(2-oxo-1,3-dioxolan-4-yl)methyl] phosphate, ethyl bis(4-formyl-2-methoxy-phenyl) phosphate, tris(5-formyl-2-methoxy-phenyl) phosphate, tris[(5-formyl-2-furyl)methyl] phosphate, tris(5-oxopentyl) phosphate, ethyl bis(3-formylphenyl) phosphate, ethyl bis(4-formylphenyl) phosphate, tris(2-furylmethyl) phosphate, tris[2-formylphenyl] phosphate, sodium bis(3-formylphenyl) phosphate, sodium bis(4-formylphenyl) phosphate, tris[4-aminophenyl] phosphate, 4-bis(4-formylphenoxy)phosphinothioyloxybenzaldehyde, tris[4-(5-hydroxy-1,3-dioxan-2-yl)phenyl] phosphate, tris(4-isocyanatophenyl) thiophosphate, sodium bis(3-formylphenyl) phosphate, tris[4-(2,5-dioxopyrrol-1-yl)phenyl] phosphate, tris(4-formyl-2-methylphenyl) phosphate, tris(4-(3-hydroxypropyl)-2-methoxyphenyl) phosphate, tris(4-(3-hydroxypropyl)-2,6-dimethoxyphenyl) phosphate, and mixtures thereof.

4- The core-shell microcapsule according to any one of the preceding claims, wherein the polyfunctional monomer is a nucleophilic polyfunctional monomer, preferably a nucleophilic polyfunctional monomer comprising nucleophilic nitrogen groups, nucleophilic sulfur groups, nucleophilic enol or phenol carbon groups, nucleophilic oxygen groups, nucleophilic phosphor groups or mixtures thereof.

5- The core-shell microcapsule according to claim 4, wherein the nucleophilic polyfunctional monomer comprises an alcohol groups, amine groups, thiol groups, enol or phenol carbon groups or mixtures thereof.

6- The core-shell microcapsule according to any one of claims 1 to 3, wherein the polyfunctional monomer is an electrophilic polyfunctional monomer, preferably an electrophilic polyfunctional monomer comprising electrophilic acyl groups, preferably acyl chloride groups, isocyanate groups, anhydride groups, aldehyde groups or mixtures thereof.

7- The core-shell microcapsule according to any one of the preceding claims, wherein the shell comprises a coacervate or coacervate-like structure comprising as first polyelectrolyte and a second polyelectrolyte, wherein the first polyelectrolyte preferably is selected from the group consisting of gum arabic, modified starch, Pectin, carboxymethyl cellulose, sodium carboxymethyl guar gum, carrageenan, lignin, plant gums, glycogen, polyaspartate, proteins and mixtures thereof and wherein the second polyelectrolyte preferably is selected from the group consisting of poly(L-lysine), animal proteins, gelatin, casein, plant proteins, chitin, chitosan, silk protein and mixtures thereof.

8- The core-shell microcapsule according to anyone of the preceding claims, wherein the hydrophobic material comprises a perfume.

9- A process for preparing a core-shell microcapsule comprising the steps of:

a) Dispersing an oil phase comprising a hydrophobic material into a continuous phase C1 to form a two-phases dispersion;

b) Optionally, dispersing the two-phases dispersion into a continuous phase C2 to form a multiple dispersion,

c) curing the dispersion obtained in step a) or in step b) to form microcapsules in the form of a slurry,

wherein a compound of formula (I) and/or a compound of formula (II), and/or a compound of formula (III) is added in the continuous phase(s) and/or in the oil phase and,

optionally, wherein a polyfunctional monomer is added in the continuous phase(s) and/or in the oil phase.

10- The process according to claim 9, wherein a stabilizer is added in the oil phase and/or in the continuous phase C1.

11- The process according to claim 10, wherein the stabilizer is selected from the group consisting of inorganic particles, polymer particles, surfactant, polymeric emulsifier such as polysaccharides, proteins, glycoproteins and mixtures thereof.

12- The process according to any one of claims 9 to 11, wherein any compound of formula (I) and/or formula (II) and/or formula (III) is added in an amount comprised between 0.01% and 10%, preferably between 0.5% and 5%, more preferably between 1% and 3% by weight, based on the total weight of the two-phases dispersion.

13- The process according to any one of claims 9 to 12, wherein the polyfunctional monomer, preferably a nucleophilic polyfunctional monomer, is added in an amount comprised between 0.1 and 10%, preferably between 0.2 and 4.0 % by weight, based on the total weight of the two-phases dispersion.

14- The process according to any one of claims 9 to 13, wherein the multiple dispersion is a two-phases dispersion, preferably an oil-in-water emulsion.

15- The process according to any one of claims 9 to 14, wherein an acid, preferably formic acid, or a base, preferably selected from the group consisting of guanidine carbonate, sodium carbonate, potassium carbonate, sodium hydroxide or mixtures thereof is added in step a) and/or b).

16- A consumer product, preferably in the form of a home-care product or personal care product or fabric care product, comprising the microcapsules as defined in anyone of claims 1 to 8.