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(54) Title: IN-SITU SOL-GEL ENCAPSULATION OF FRAGRANCES, PERFUMES OR FLAVOURS

(57) Abstract: The invention relates to microcapsules having a core material encapsulated within a microcapsular shell, said core material comprises at least one active ingredient selected from the group consisting of fragrance, perfume, aromas and flavour, wherein the microcapsular shell comprises at least one inorganic/hybrid material obtained by in-situ sol-gel polymerization of said precursors; wherein the concentration of the core material based on total weight of the microcapsules is less than 80 weight-%, and a process for preparing the microcapsules.



In-situ Sol-Gel Encapsulation of Fragrances, Perfumes or Flavours

Field of the invention

The present invention generally relates to a method of encapsulating fragrances, per-
fumes, aromas or flavour into microcapsules having an inorganic hybrid shell and an
5 oily core.

Background of the Invention

Most consumers expect scented laundry products and fabrics which have been laun-
10 dered also have a pleasing fragrance. The consumer products industry has searched
for methods to enhance the fragrance performance of commercial products such as
liquid soap, body wash, laundry detergents, shampoos, conditioners, surface cleaners,
and particularly for fabric care products. Fragrance typically are added to fabric care
products to provide a fresh, clean impression for the product itself, as well as to the
15 fabric treated with the product. Although the fragrance does not enhance the perform-
ance of a fabric care product, the fragrance makes these products more aesthetically
pleasing, and consumers expect and demand a pleasing odour for such products.

Introduction of a fragrance into substrate, such as via a fabric care product, is restricted
20 by consideration such as availability and cost, and also by an inability of the fragrance
to sufficiently deposit onto the substrate, and then remain on the substrate for an ex-
tended period of time. Fabric care products, particularly, should remain on the fabric
during the wash, rinse, and drying cycles. It has been demonstrated that a substantial
amount of the fragrance in currently available fabric care products is lost during
25 wash/rinse cycles. This fragrance loss is attributed to the water solubility of various
fragrance ingredients, to the volatility of fragrance ingredients that deposit on the fabric,
and the wash-off of the fragrance from the fabric.

Fragrances, perfumes or flavours are an essential additive in consumer products such
30 as household detergent and laundry products. They provide the control of odour. Deliv-
ery of fragrances from detergents onto fabric is a challenge for the fabric-care industry.

Perfumers have a portfolio of approx. 2000 fragrance raw materials (including solvents
and emulsifiers). Fragrance ingredients are from different chemical groups. Main
35 chemical categories are alcohols, aldehydes, esters, ketones, lactones, acids, acetals,
ethers, aromatics, schiff bases.

The majority of laundry detergent and cleaning product compositions comprise fra-
grances or perfumes in order to impart a pleasant fragrance to the compositions them-
selves or to the surfaces or textiles they are used to treat. Said fragrances, perfumes or
40 flavours are usually compounds having two or more conjugated double bonds which
are more or less sensitive to various chemicals or to oxidation. Consequently, there

may be unwanted interactions with other ingredients of the detergents or cleaning products, such as surfactants or bleaches, for example, as a result of which the perfume is decomposed and/or the odour note is altered. Another problem is the occasionally high volatility of the fragrances or perfumes, which means that a large part of the quantity of perfume originally admixed to the detergent or cleaning product has escaped before the time of use.

Attempts have been made to increase fragrance storage stability, deposition onto fabric, and to hinder or delay the release of the fragrance from the fabric, such that the laundered fabric remains esthetically pleasing for an extended length of time. One solution to overcome the problem is to incorporate the fragrances or perfumes in nano-, micro-encapsulated form into the detergents or cleaning products.

Microcapsules incorporating a flavour, perfume or fragrance compound are useful to provide storage stability and a controlled release of the contained flavour, perfume or fragrance.

Various routes are available based on methods such as spray-drying, spray-cooling/chilling, spinning disk and centrifugal coextrusion, extrusion, fluidized bed, coacervation, alginate beads, liposome, supercritical solution and inclusion encapsulation.

U. S. Patent No. 6,790,814 discloses that a fragrance loaded into a porous carrier material, such as Zeolite particles, can be effectively protected from premature release of the fragrance by coating the loaded carrier particles with hydrophobic oil, then encapsulating the resulting carrier particles with a water-soluble or water-dispersible, but oil-insoluble material such as starch or modified starch.

U.S. Patent Nos. 4,946,624; 5,112,688; 5,126,061 and 4,402,856 disclose microcapsules prepared by a coacervation process. The microcapsules have a complex structure, with a large central core of encapsulated material, preferably a fragrance, and walls that contain small wall inclusion particles of either the core material or another material that can be activated to disrupt them all for release of fragrance. Coacervation technique provides fragrance particles for fabric care products containing gelatine or a mixture of gelatine with gum Arabic, carboxymethylcellulose, and/or anionic polymers. The microcapsules are incorporated into a fabric softener composition having a pH of about 7 or less and which further contains a cationic fabric softener. The microcapsules are added separately to the fabric softener compositions. This type of controlled release system cannot be used with all types of fragrance ingredients, in particular, with fragrance ingredients that are relatively water soluble and/or incapable of deposition onto a fabric.

U. S. Patent Nos. 4,152,272; 4,973,422; and 5,137,646 disclose incorporating a fragrance into wax particles to protect the fragrance during storage and through the laundry process. The particles further can be coated with a material that renders the particles more substantive to the surface being treated. The particles comprise a fragrance dispersed within a wax material. In general the coating materials are water-insoluble cationic materials. The load of fragrance or other active agent is limited to about 30% by weight, of the waxy material. The fragrance/wax particles are incorporated into an aqueous fabric conditioner composition. The fragrance diffuses from the particles into the fabric in the heat-elevated conditions of the dryer.

WO 2005/009604 and WO 2008/072239 disclose in-situ sol-gel encapsulation and exemplify encapsulation of UV-absorbers and dyes. The microcapsules have a microcapsular shell comprising at least one inorganic polymer comprising polymerized precursors obtained by in-situ polymerization of the precursors.

Thus, there is a need for an efficient method of adsorbing the many types of perfumes, flavour and fragrance compounds to the desired level of loading in an encapsulated oil.

The present invention provides an alternative encapsulation method which offers certain advantages over those techniques known in the prior art. An in-situ sol-gel method based on emulsion provides core-shell microcapsules, wherein the core material comprises at least one fragrance, perfume or flavour ingredient; the shell of the microcapsule comprises at least one inorganic and/or hybrid material. Therefore, it is an object of the present invention to provide an encapsulation process resulting in encapsulated particles with a spherical and uniform coating substantially free of surface imperfections adversely affecting barrier properties in a liquid medium.

Summary of the Invention

This invention relates to microcapsules and a method of encapsulating a fragrance, perfume or flavour compound by in-situ sol-gel and emulsion processes. The sol-gel process can be regarded as the inorganic analogue of interfacial polymerization encapsulation. During the sol-gel encapsulation, an inorganic gel network is formed by gelation of a sol (a colloidal suspension). The most commonly used precursors are metal alkoxides or semi metal alkoxides, which can react and undergo the sol-gel transition in aqueous environment.

The present invention relates to compositions comprising an inorganic shell and a core incorporating at least one fragrance, perfume or flavour. The compositions can further include external cationic modification as deposition aids. The compositions described herein can be used in cleansing products, such as shampoos, conditioners, body washes, moisturizing agents, creams, shower gels, soaps, detergents, surface cleansing agents, and surface-conditioning agents, such as fabric softeners.

The present invention generally relates to a method for the preparation of microcapsules and the resulting products – the microcapsules.

- 5 The main object of the instant invention is directed to microcapsules having a core material encapsulated within a microcapsular shell, said core material comprises at least one active ingredient selected from the group consisting of fragrance, perfume and flavour, and wherein the microcapsular shell comprises at least one inorganic and/or hybrid material obtained by in-situ sol-gel polymerization of said precursors; wherein
10 the concentration of the core material based on total weight of the microcapsules is less than 80 weight-%.

A hybrid material is a mixture network comprising of inorganic and organic components. Included are inorganic-organic polymers and organic-inorganic polymers.

15

In the instant invention the terms aroma, fragrance, perfume and flavour mean at least one compound or composition having a pleasant, agreeable scent or odour or a smell or a taste.

- 20 In a preferred embodiment of the instant invention the microcapsules having as core material at least one active ingredient selected from the group consisting of fragrance, perfume and flavour and hydrophobic material, such as at least one non-polar solvent.

A further object of the instant invention is directed to a process for preparing microcapsules having a core material encapsulated within a microcapsular shell, said core material comprises at least one active ingredient selected from the group consisting of fragrance, perfume and flavour, wherein the concentration of the core material based on total weight of the microcapsules is less than 80 weight-%,
25 said process comprises the step of

- 30 (a) preparing a mixture of the hydrophobic material, such as at least one non-polar solvent, at a certain temperature and at least one sol-gel precursor and at least one fragrance perfume and/or flavour;
(b) preparing an oil-in-water emulsion by emulsification of an oily phase that comprises the core material, in an aqueous phase, under high shear forces, wherein the oily
35 phase comprises at least one sol-gel precursor;
(c) applying conditions for the sol-gel process to obtain nano- or micro-capsules having a metal oxide or inorganic-organic hybrid shell encapsulating the core material, said capsules most preferably have an average particle size of less than 2 μm ; and
(d) optionally introducing external cationic materials e.g. polymers, surfactants or colloids to modify the surface of the shell, in order to improve the deposition of microcapsules on the surface.
40

- A preferred embodiment of the instant invention is directed to a process for preparing microcapsules having a core material encapsulated within a microcapsular shell, said core material comprises at least one active ingredient selected from the group consisting of fragrance, perfume and flavour and hydrophobic material, such as at least one
- 5 non polar organic solvent, wherein the concentration of the core material based on total weight of the microcapsules is less than 80 weight-%, said process comprises the step of
- (a) preparing a mixture of the hydrophobic material, such as wax at a certain temperature and at least one sol-gel precursor and at least one fragrance perfume and/or flavour;
- 10 (b) preparing an oil-in-water emulsion by emulsification of an oily phase that comprises the core material, in an aqueous phase, under high shear forces, wherein the oily phase comprises at least one sol-gel precursor;
- (c) applying conditions for the sol-gel process to obtain nano- or micro-capsules having
- 15 a metal oxide or inorganic-organic hybrid shell encapsulating the core material, said capsules have in a preferred embodiment a particle size distribution of: $d_{50} = 0.2 - 1 \mu\text{m}$, in diameter; and
- (d) optionally introducing external cationic materials e.g. polymers, surfactants or colloids to modify the surface of the shell, in order to improve the deposition of microcapsules on the surface.
- 20

Hydrophobic materials which can be used are in principle all substances or mixtures which can be emulsified in water at temperatures between their melting point and the boiling point of water. They include all kinds of oils, such as vegetable oils, animal oils,

25 mineral oils, paraffins, chlorinated paraffins, fluorocarbons, and other synthetic oils. Typical examples are sunflower oil, rapeseed oil, olive oil, peanut oil, soya oil, kerosine, benzene, toluene, butane, pentane, hexane, cyclohexane, chloroform, carbon tetrachloride, chlorinated biphenyls, and silicone oils. It is also possible to use high boiling point hydrophobic materials, examples being diethyl phthalate, dibutyl phthalate, diisohexyl phthalate, dioctyl phthalate, alkylnaphthalenes, dodecylbenzene, terphenyl, and

30 partially hydrogenated terphenyls. Polymers can also be used as hydrophobic core material provided they are emulsifiable in water. This proviso is generally met when the glass transition temperature of the polymers is below the temperature at which the polymers are emulsified in water. Examples of such polymers are homopolymers or

35 copolymers of C_1 - C_{20} alkyl acrylates, homopolymers or copolymers of C_3 - C_{20} methacrylates, copolymers of styrene and styrene derivatives with acrylates or methacrylates, polyesters, oligomeric polyolefins based on ethylene, propylene or isobutylene, polyamides, and polycarbonates having a hydrophobic character. Suitable examples are polybutyl acrylate, polyethylhexyl acrylate, poly(styrene-co-n-butyl acrylate) and

40 cold-polymerized poly(styrene-co-butadiene). Mixtures of two or more of the materials described, and mixtures of low molecular mass hydrophobic materials with water-

emulsifiable polymers, can also be used as the hydrophobic material.

A more preferred embodiment of the instant invention is directed to microcapsules and a process for their manufacture, wherein the hydrophobic material such as non polar
5 organic solvent is selected from the group consisting of waxes, vegetable oil, mineral oil or mixtures thereof.

Chemically, a wax is a type of lipid that may contain a wide variety of long-chain alkanes, esters, polyesters and hydroxy esters of long-chain primary alcohols and fatty
10 acids. They are usually distinguished from fats by the lack of triglyceride esters of glycerin (propan-1,2,3-triol) and three fatty acids. In addition to the esters that contribute to the high melting point and hardness of carnauba wax, the epicuticular waxes of plants are mixtures of substituted long-chain aliphatic hydrocarbons, containing alkanes, fatty acids, primary and secondary alcohols, diols, ketones, aldehydes. The nature of the
15 other lipid constituents can vary greatly with the source of the waxy material, but they include hydrocarbons, sterol esters, aliphatic aldehydes, primary and secondary alcohols, diols, ketones, β -diketones, triacylglycerols, and many more.

A number of waxes are produced commercially in large amounts for use in cosmetics,
20 lubricants, polishes, surface coatings, inks and many other applications. Some of these are of mineral origin (e.g. montan wax from brown coal/peat deposits), and only those from living organisms are discussed here. Amongst them are:

Beeswax - Glands under the abdomen of bees secrete a wax, which they use to construct the honeycomb. The wax is recovered as a by-product when the honey is harvested and refined. It contains a high proportion of wax esters (35 to 80%). The hydrocarbon content is highly variable, and much may be "unnatural" as beekeepers may feed some to bees to improve the yield of honey. The wax esters consist of C40 to C46
25 molecular species, based on 16:0 and 18:0 fatty acids some with hydroxyl groups in the ω -2 and ω -3 positions. In addition, some diesters with up to 64 carbons may be present, together with triesters, hydroxy-polyesters and free acids (which are different in composition and nature from the esterified acids).
30

Jojoba - The jojoba plant (*Simmondsia chinensis*), which grows in the semi-arid regions of Mexico and the U.S.A., is unique in producing wax esters rather than triacylglycerols in its seeds, and it has become a significant crop. It consists mainly of 18:1 (6%), 20:1 (35%) and 22:1 (7%) fatty acids linked to 20:1 (22%), 22:1 (21%) and 24:1 (4%) fatty alcohols. Therefore, it contains C38 to C44 esters with one double bond in each alkyl moiety. As methylene-interrupted double bonds are absent, the wax is relatively resistant to oxidation.
40

Carnauba - The leaves of the carnauba palm, *Copernicia cerifera* that grows in Brazil, have a thick coating of wax, which can be harvested from the dried leaves. It contains mainly wax esters (85%), accompanied by small amounts of free acids and alcohols, hydrocarbons and resins. The wax esters constitute C16 to C20 fatty acids linked to C30 to C34 alcohols, giving C46 to C54 molecular species.

Other vegetable "waxes" such as bayberry or Japan wax are better described as "tallows" as they consist mainly of high melting triacylglycerols.

Wool wax (lanolin) - The grease obtained from the wool of sheep during the cleaning or refining process is rich in wax esters (of 1- and 2-alkanols, and 1,2-diols), sterol esters, triterpene alcohols, and free acids and sterols. The nature of the product varies with the degree and type of processing involved, but can contain up to 50% wax esters and 33% sterol esters. A high proportion of the sterol component is lanosterol. The fatty acid components are mainly saturated and iso- and anteiso-methyl-branched-chain.

In addition, there is a number of Plant Surface Waxes. Plant leaf surfaces are coated with a thin layer of waxy material that has a myriad of functions. This layer is microcrystalline in structure and forms the outer boundary of the cuticular membrane; it is the interface between the plant and the atmosphere. It serves many purposes, for example to limit the diffusion of water and solutes, while permitting a controlled release of volatiles that may deter pests or attract pollinating insects. The wax provides protection from disease and insects, and helps the plants resist drought. As plants cover much of the earth's surface, it seems likely that plant waxes are the most abundant of all natural lipids.

The major constituents of plant leaf waxes are n-Alkanes, Alkyl esters, Fatty acids, Fatty alcohols (primary), Fatty aldehydes, Ketones, Fatty alcohols (secondary), β -Diketones, Triterpenols (Sterols, α -amyrin, β -amyrin, uvaol, lupeol, erythrodiol) and Triterpenoid acids (Ursolic acid, oleanolic acid, etc). Besides, there may be hydroxy- β -diketones, oxo- β -diketones, alkenes, branched alkanes, acids, esters, acetates and benzoates of aliphatic alcohols, methyl, phenylethyl and triterpenoid esters, and many more.

Preferably the waxes are petroleum waxes, e.g. paraffin wax - made of long-chain alkane hydrocarbons, microcrystalline wax - with very fine crystalline structure and synthetic waxes, e.g. polyethylene waxes - based on polyethylene, Fischer-Tropsch waxes, chemically modified waxes - usually esterified or saponified, substituted amide waxes.

Preferably the waxes are mixable with precursors and have a melting point at 30- 80°C, more preferably having a melting point at 40- 60°C.

More preferred waxes are animal waxes, such as e.g. beeswax, lanolin (wool wax) or shellac wax, vegetable waxes, such as e.g. carnauba wax, soy wax or castor wax, mineral waxes, such as e.g. montan waxes, peat waxes or ceresin waxes, petroleum waxes, such as e.g. paraffin wax or microcrystalline wax, or synthetic waxes, such as
5 e.g. polyethylene waxes, Fischer Tropsch waxes, chemically modified (esterified or saponified) waxes or amide waxes, and polymerized α -olefins, or mixtures thereof.

Vegetable oils which can be used in the instant invention are e.g. coconut oil, olive oil, peanut oil, soybean oil, sunflower oil, cashew oil, hazelnut oil, pistachio oil, walnut oil,
10 Borneo tallow nut oil, pine nut oil.

Mineral oils which can be used in the instant invention are e.g. paraffinic oils, naphthenic oils, aromatic oils, adepsine oil.

15 The oily core may comprise, for example, wax, vegetable oil, mineral oil, or mixtures thereof and at least one fragrance, perfume or flavour. As more particularly defined hereinafter, "oil" is meant to include a wide range of substance that is dispersible in water due to their hydrophobic nature.

20 The shell of the microcapsules of the instant invention preferably consists of at least one (semi)metal oxide material. As (semi)metal oxides there are preferred SiO_2 , ZnO , Al_2O_3 or TiO_2 . SiO_2 is mostly preferred.

The precursors used in the present invention to build the microcapsular shell are preferably precursors selected from silicon alkoxides monomers, silicon ester monomers and monomers of the formula $\text{Si}(\text{R}_1)_n(\text{R}_2)_m$, wherein R_1 is a hydrolysable substituent, n is an integer from 2 to 4, R_2 is a non polymerizable substituent and m is an integer from 0 to 4, a partially hydrolyzed and partially condensed polymer thereof, and mixtures thereof. The expression "hydrolyzable substituent" means a substituent eliminated by
25 hydrolysis in the same conditions, such as an alkoxy group.
30

The precursors more preferably are mixtures of $\text{SiR}_3(\text{OR}_4)_3$ and $\text{Si}(\text{OR}_5)_4$, wherein R_3 , R_4 and R_5 is independently from one another C_1 - C_6 alkyl. Examples are methyl, ethyl, n-propyl, isopropyl, sec-butyl, tert-butyl, isobutyl, n-butyl, n-pentyl and n-hexyl.
35

Preferably the ratio between $\text{SiR}_3(\text{OR}_4)_3$ and $\text{Si}(\text{OR}_5)_4$ is in the range of 1:10- 1:1, more preferably of 1:6- 1:3.

In a preferred embodiment of the instant invention the precursors are selected from the
40 mixture of the compounds methyltrimethoxysilane (MTMS) and tetraethoxysilane (TEOS), methyltriethoxysilane (MTES) and tetraethoxysilane (TEOS), methyltrimethoxysilane (MTMS) and tetramethoxysilane (TMOS), methyltriethoxysilane (MTES) and

tetramethoxysilane (TMOS), n-propyltriethoxysilane (n-PTES) and tetramethoxysilane (TMOS), n-propyltriethoxysilane (n-PTES) and tetraethoxysilane (TEOS).

5 In a very much preferred embodiment of the instant invention the precursors are selected from the mixture of the compounds methyltriethoxysilane (MTES) and tetraethoxysilane (TEOS).

10 The invention is also directed to the products produced by the methods of the invention. Microcapsules have a core material encapsulated within a shell of the microcapsule; said core material comprises at least one active ingredient selected from the group consisting of fragrance, perfume and flavour and hydrophobic material, such as at least one non polar organic solvent, preferably at least one wax, wherein the shell of the microcapsule comprises at least one inorganic or hybrid polymer comprising polymerized precursors obtained by in-situ polymerization of said precursors; wherein the
15 concentration of the core material based on total weight of the microcapsules is less than 80 weight-%.

20 One advantage of the invention is that the microcapsule may contain a concentration of the fragrance or flavour compound in either a liquid or gaseous state. A second advantage is the increased yield of encapsulated fragrance, perfume or flavour, since they should be maintained in oil phase well. Another advantage is the positively charge surface, which provide a better deposition to a fabric. The process is also environmentally friendly and bio-compatible.

25 The present invention relates to microcapsules having a core material encapsulated within a microcapsular shell, said core material comprises at least one active ingredient, wherein the microcapsular shell comprised at least one inorganic or hybrid material.

30 Preferably the core consists essentially of at least one active ingredient. The core material comprises a high percentage of an active ingredient and low percentage of excipients (such as the liquid carrier). Preferably the concentration of the active ingredient based on the total weight of the core is above 20% w/w, more preferably above 40% w/w. 20% w/w means that the mass of the substance is 20% of the total mass of the
35 solution or mixture.

40 Microcapsules have an average particle diameter less than about 100 μm , preferably less than about 50 μm , more preferably less than about 10 μm , and most preferably less than about 4 μm . The average particle size of the microcapsules of the invention especially preferred is between 0.2 μm and 2 μm .

Fragrance particulates are liquid, solid, and mixtures of these. As used herein the term fragrances, perfumes or flavours refers to any applicable material that is sufficiently volatile to produce a scent. Typically, fragrances are those scents pleasurable to humans, alternatively fragrances are those scents repellent to humans, animals, and insects. Suitable fragrances include but are not limited to fruits such as almond, apple, cherry, grape, pear, pineapple, orange, strawberry, raspberry, musk, and flower scents. Other fragrances include herbal scents such as rosemary, thyme, and sage; and woodland scents derived from pine, spruce and other forest smells. Fragrance may also be derived from various oils, such as essential oils, or from plant material such as peppermint, spearmint and the like. Fragrances can be familiar and popular smells such as baby powder, popcorn, pizza, cotton candy and the like, or can be medicinal smells and analgesics.

The fragrance particulates applicable herein are generally not for human consumption that is non-edible. Herein, non-edible means that the U.S. Food and Drug Administration regulates, prohibits, or has not expressly provides for their consumption. Preferably, the fragrance, perfume or flavour used herein is hydrophobic. Herein, hydrophobic means that the fragrance and water visibly phase separate when combined without agitation.

In preferred microcapsules according to the instant invention the active ingredient is selected from the group consisting of hydrophobic fragrance, perfume and flavour.

The term fragrance or perfume refers to all organic substances which have a desired olfactory property and are essentially nontoxic. They include all perfumes or fragrances commonly used in laundry detergent or cleaning product compositions or in perfumery. They can be compounds of natural, semisynthetic, or synthetic origin. Preferred fragrances or perfumes can be assigned to the classes of the hydrocarbons, aldehydes or esters. The fragrances or perfumes also include natural extracts and/or essences which may comprise complex mixtures of constituents, such as orange oil, lemon oil, rose extract, lavender, musk, patchouli, balsam essence, sandalwood oil, pine oil, and cedar oil.

Nonlimitative examples of synthetic and semisynthetic fragrances and perfumes are: 7-acetyl-1,2,3,4,5,6,7,8-octahydro-1,1,6,7-tetramethyl-naphthalene, .alpha.-ionone, .beta.-ionone, .gamma.-ionone .alpha.-isomethylionone, methylcedrylone, methyl dihydrojasmonate, methyl 1,6,10-trimethyl-2,5,9-cyclododecatrien-1-yl ketone, 7-acetyl-1,1,3,4,4,6-hexamethyltetralin, 4-acetyl-6-tert-butyl-1,1-dimethylindane, hydroxyphenylbutanone, benzophenone, methyl .beta.-naphthyl ketone, 6-acetyl-1,1,2,3,3,5-hexamethylindane, 5-acetyl-3-isopropyl-1,1,2,6-tetramethylindane, 1-dodecanal, 4-(4-hydroxy-4-methylpentyl)-3-cyclohexene-1-carboxaldehyde, 7-hydroxy-3,7-dimethyloctanal, 10-undecen-1-al, isohexenylcyclohexylcarboxaldehyde, formyltricy-

clodecane, condensation products of hydroxycitronellal and methyl anthranilate, condensation products of hydroxycitronellal and indole, condensation products of phenylacetaldehyde and indole, 2-methyl-3-(para-tert-butylphenyl)propionaldehyde, ethylvanillin, heliotropin, hexylcinnamaldehyde, amylcinnamaldehyde, 2-methyl-2-
 5 (isopropylphenyl)propionaldehyde, coumarin, .gamma.-decalactone, cyclopentadecanolide, 16-hydroxy-9-hexadecenoic acid lactone, 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl-cyclopenta-.gamma.-2-benzopyran, .beta.-naphthol methyl ether, ambroxane, dodecahydro-3a,6,6,9a-tetramethylnaphtho[2,1b]furan, cedrol, 5-(2,2,3-trimethylcyclopent-3-enyl)-3-methylpentan-2-ol, 2-ethyl-4-(2,2,3-trimethyl-3-
 10 cyclopenten-1-yl)-2-buten-1-ol, caryophyllene alcohol, tricyclodecenyl propionate, tricyclodecenyl acetate, benzyl salicylate, cedryl acetate, and tert-butylcyclohexyl acetate.

Particular preference is given to the following: hexylcinnamaldehyde, 2-methyl-3 (tert-butylphenyl)-propionaldehyde, 7-acetyl-1,2,3,4,5,6,7,8-octahydro-1,1,6,7-
 15 tetramethylnaphthalene, benzyl salicylate, 7-acetyl-1,1,3,4,4,6-hexamethyltetralin, para-tert-butylcyclohexyl acetate, methyl dihydrojasmonate, .beta.-naphthol methyl ether, methyl .beta.-naphthyl ketone, 2-methyl-2-(para-isopropylphenyl)propionaldehyde, 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-.gamma.-2-benzopyran, dodecahydro-3a, 6,6,9a-
 20 tetramethylnaphtho[2,1b]furan, anisaldehyde, coumarin, cedrol, vanillin, cyclopentadecanolide, tricyclodecenyl acetate and tricyclodecenyl propionates.

Other fragrances are essential oils, resinoids and resins from a large number of sources, such as, for example, Peru balsam, olibanum resinoid, styrax, labdanum
 25 resin, nutmeg, cassia oil, benzoin resin, coriander, and lavandin. Further suitable fragrances include: phenylethyl alcohol, terpeneol, linalool, linalyl acetate, geraniol, nerol, 2-(1,1-dimethylethyl)cyclohexanol acetate, benzyl acetate, and eugenol.

Flavour is the sensory impression of a substance and is determined mainly by the
 30 chemical senses of taste and smell. The U.S. Code of federal Regulations describes a "natural flavouring" as: the essential oil, oleoresin, essence or extractive, protein hydrolysate, distillate, or any product of roasting, heating or enzymolysis, which contains the flavouring constituents derived from a spice, fruit or fruit juice, vegetable or vegetable juice, edible yeast, herb, bark, bud, root, leaf or any other edible portions of a plant,
 35 meat, seafood, poultry, eggs, dairy products, or fermentation products thereof, whose primary function in food is flavouring rather than nutritional. Examples for a smell are: diacetyl has a buttery odour; ethyl propionate has a fruity odour; limonene has an orange odour; ethyl vanillin has a vanilla odour. Examples for a taste are: citric acid gives fruits their sour taste; tartaric acid gives grapes their tart taste.

40

The terms fragrance, scent, and also aroma are used primarily by the food and cosmetic industry to describe a pleasant odour, and are also used to refer to perfumes.

The term aroma is also known as odorant, fragrance or flavour. Aroma is chemically a compound that has a smell or odour. An aroma compound has to fulfill two conditions: the compound needs to be volatile, so it can be transported to the olfactory system of the nose, and it needs to be in a sufficiently high concentration to be able to interact with one or more of the olfactory receptors.

Aroma compounds can be found in food, wine, spices, perfumes, fragrance oils, and essential oils. In wines, most form as byproducts of fermentation. As well many of the aroma compounds plays a significant role in the production of flavorants, which are used in the food service industry to flavor, improve and increase the appeal of their products.

Some examples of aroma compounds are: methyl butyrate, nerol, citral, citronellal, linalool, limonene, camphor, cinnamaldehyde, vanillin, pyridine, menthol, hexyl acetate

The fragrance, perfume or flavour can be used as single substance or in a mixture with one another. The fragrance or perfume may, as the sole hydrophobic material, form the core of the microcapsules. Alternatively, the microcapsules may in addition to the fragrance or perfume include a further hydrophobic material in which the fragrance or perfume is dissolved or dispersed. For example, when using fragrances or perfumes which are solid at room temperature, the use of a hydrophobic material which is liquid at room temperature, as a solvent or dispersant is advantageous. Similarly, oil may be added to the fragrance or perfume in order to increase its hydrophobicity.

The fragrance or perfume, or the mixture of fragrances or perfumes, preferably accounts for from 1 to 100% by weight, in particular from 20 to 100% by weight, of the hydrophobic core material.

In a preferred embodiment of the instant invention core material (fragrance, perfume or flavour) is used which in addition may contain an emulsifier.

In a preferred embodiment of the instant invention the concentration of the core material based on the total weight of the microcapsules is less than 60 weight-percent (weight-%), more preferred less than 50 weight-%, and most preferred within the range of 10 to 49 weight-%.

In a further preferred embodiment of the instant invention said core material is a liquid core, more preferred a liquid oily core.

Preferably the core is a liquid core and more preferably the liquid core is a liquid oily core. Preferably the liquid core is a solution, suspension or dispersion and more pref-

erably the liquid core is an oily core for examples in the form of a solution, suspension or dispersion. The active ingredient may be present in a dissolved, dispersed or suspended form in the core.

- 5 The active ingredient may be any fragrance, perfume or flavour molecule that are soluble or that can be suspended in the precursor (metal or semimetal alkoxides) of choice.

Preferably emulsifiers used in the core material are cationic surfactants of the formula



- wherein R', R'', R''' and R'''' independently from one another is C₁-C₂₀alkyl and X is halogen, such as e.g. chlorine and bromine; preferably X is chlorine. In a more preferred emulsifier of the above given formula R' is C₈-C₁₈alkyl and R'', R''' and R'''' is
15 independently from one another methyl and X is chlorine, such as e.g. cetyltrimethylammonium chloride (CTAC).

- According to one embodiment the conditions in step (c) comprising adding a catalyst to accelerate the formation of the microcapsular shell for example, by adding an acid or
20 base.

- Thus, according to a preferred embodiment the conditions in step (c) comprising adding a catalyst selected from an acid or base. In a preferred embodiment the acid is added to provide the emulsion a pH in the range 1-7.

- 25 An emulsion is obtained by shearing a mixture comprising two immiscible liquid phases.

- The shearing proceeds usually via rotor-stator, ultrasonication of the mixture or with a high-pressure homogenizer, which are high-shearing processes.

- Ultrasonication is known to offer potential in the processing of liquids and slurries, by improving the mixing and chemical reactions in various applications. Ultrasonication is an alternative to high-speed mixers. Ultrasonication generates strong hydrodynamic
35 shear-forces.

- The conditions in step (c) may comprise for mixing and stirring the emulsion with another aqueous solution at suitably selected pH in the range of 2 to 6, preferably to obtain a pH of 3 to 5 of the emulsion.

The conditions in step (c) may comprise the adjustment of solution pH for condensation. The pH is adjusted to be in the range of 5 to 7, preferably to obtain a pH of around 6 of the emulsion.

- 5 The mixing in step (c) may be conducted for at least 3 hours, typically 5- 20 hours.

The mixing temperature is maintained in the range of 0- 100°C, preferably in the range of 10- 60°C, more preferably in the range of 20- 40°C.

- 10 The process of the present invention may further comprise the step of rinsing the capsules through centrifuge, filtration, evaporation, re-suspension in an aqueous medium and dialysis.

- 15 The suspension so obtained may be stabilized by adding additives such as non-ionic, cationic or anionic polymers or surfactants or mixtures thereof.

The process may further comprise the step of removing the water to obtain the final product in a powder form.

- 20 Capsules of the present invention are physically stable for a period of time of at least 8 weeks, in an aqueous medium substantially free of surfactants, at ambient conditions (0- 50°C), with an increase of about 10% in particle size parameters.

- 25 The concentration of the oily phase in the emulsion may be in the range of 5% to 50% w/w, more preferable in the range of 20- 40%.

- The concentration of the core material based total weight of the capsules may be from 10% to 80% w/w. According to specific embodiment the concentration of the core material based total weight of the capsules is from 20% to 60% w/w.

- 30 The shell may be further modified by functional groups selected from C₁-C₁₈alkyl, aryl, C₁-C₁₈alkyl amine, C₁-C₁₈alkyl methacrylate, haloC₁-C₁₈alkyl, allyl, vinyl, C₁-C₁₈alkyl ester, acryloxy, allyloxy, aryloxy, carboxyC₁-C₁₈alkyl, C₁-C₁₈alkyl(C=O)-O-, cyanoC₁-C₁₈alkyl, epoxycycloalkyl, glycidoxyc₁-C₁₈alkyl, methacryloxy, C₁-C₁₈alkylthiol.

- 35 In certain applications it may be desired to achieve a controlled release of the active ingredient selected from the group consisting of fragrances, perfumes or flavours from the microcapsules. The possible release mechanisms are mechanical release through breaking shell, temperature release through melt wax, slow release through diffusion.

- 40 In most applications slow release is desired.

Examples

The following examples demonstrate the present invention. They are not under any circumstances exclusive and do not intend to limit the scope of the present invention.

Abbreviations used: MTES = methyltriethoxysilane; n-PTES = n-propyltriethoxysilane;

5 TEOS = tetraethoxysilane; CTAC = cetyltrimethyl ammonium chloride.

Example 1:

Citronellynitril of BASF SE (CAS Reg.-Nr. 51566-62-2) in Luwax V:

10 g of a commercial polyvinylether wax (Luwax V of BASF SE) was dissolved into 5 g
10 MTES and 15 g TEOS solution at 60°C. 10 g Citronellynitril was immediately poured
into the above oil phase. 200 g water solution of 0.88 g cationic surfactant CTAC (2.5%
of oil phase) was heated at around 60°C. The oil phase was mixed with the water
phase using an Ultrasonic stab (200 w, 13 mm) for 2 min. The pH of the emulsion was
adjusted with 2 mL 0.1M NH₄OH from approx. 3.5 to 6.0. The final emulsion was trans-
15 ferred to 500 mL beaker equipped with magnetic stirrer (350 rpm). The emulsion was
stirred at 40°C for 16 h for the aging of the shell.

The particle size distribution (PSD) was measured by Bluewave (Microtrac S3500
Bluewave, Microtrac) and the results were: d₅₀= 0.5 µm.

20 The core-shell structure was recognized with the Transmission electron microscope
(TEM) measurements. The shell was broken with vacuum drying.

The theoretical loading of Citronellynitril is approx. 38%. The loading of Citronellynitril
was determined by Thermogravimetric (TGA) Measurement. The weight difference of
the spray dried sample between 130°C (water should be evaporated completely, to-
gether with unencapsulated perfume) and 300°C (the decomposition temperature for
25 Luwax V is 350°C) is approx. 30%. It means that the loading of the encapsulated Citro-
nellynitril should be at least 30%.

Example 2:

Citronellynitril of BASF SE (CAS Reg.-Nr. 51566-62-2) in Paraffin wax:

30 10 g of a commercial Paraffin wax (Fa. Aldrich, CAS 8002-74-2) was dissolved into 5 g
MTES and 15 g TEOS solution at 55°C. 10 g Citronellynitril was immediately poured
into the above oil phase. 200 g water solution of 0.88 g cationic surfactant CTAC (2.5%
of oil phase) was heated at around 55°C. The oil phase was mixed with the water
phase using an Ultrasonic stab (200 w, 13 mm) for 2 min. The pH of the emulsion was
35 adjusted with 2 mL 0.1M NH₄OH from approx. 3.5 to 6.0. The final emulsion was trans-
ferred to 500 mL beaker equipped with magnetic stirrer (350 rpm). The emulsion was
stirred at 40°C for 16 h to age the shell.

The particle size distribution (PSD) was measured by Bluewave (Microtrac S3500 Bluewave, Microtrac) and the results were: $d_{50} = 0.5 \mu\text{m}$.

The theoretical loading of Citronellynitril is approx. 38 wt-%. The loading of the Citronellynitril was determined by TGA Measurement. The weight difference of the spray dried sample between 130°C (water should be evaporated completely, together with unencapsulated perfume) and 300°C (the decomposition temperature for Paraffin wax is at least 300°C) is approx. 25 wt-%. It means that the loading of encapsulated Citronellynitril should be at least 25 wt-%.

10 Example 3:

Linalylacetat of BASF SE (CASNo : 115-95-7) in Luwax V:

10 g of a commercial polyvinylether wax (Luwax V of BASF SE) was dissolved into 5 g MTES and 17 g TEOS solution at 60°C. 8 g Linalylacetat was immediately poured into the above oil phase. 200 g water solution of 0.8 g cationic surfactant CTAC (2.0% of oil phase) was heated at around 60°C. The oil phase was mixed with the water phase using an Ultrasonic stab (200 w, 13 mm) for 2 min. The pH of the emulsion was adjusted with 2 mL 0.1M NH_4OH from approx. 3.7 to 6.0. The final emulsion was transferred to 500 mL beaker equipped with magnetic stirrer (350 rpm). The emulsion was stirred at 40°C for 12 h to age the shell.

20 The particle size distribution (PSD) was measured by Bluewave (Microtrac S3500 Bluewave, Microtrac) and the results were: $d_{50} = 0.8 \mu\text{m}$.

The theoretical loading of Linalylacetat is approx. 32%. The loading of the Linalylacetat was determined by TGA Measurement. The weight difference of the spray dried sample between 130°C and 300°C is approx. 20%. It means that the loading of encapsulated Linalylacetat should be at least 20%.

Example 4:

Linalylacetat of BASF SE (CASNo : 115-95-7) in Paraffin wax:

10 g of a commercial Paraffin wax (Fa. Aldrich, CAS 8002-74-2) was dissolved into 5 g MTES and 17 g TEOS solution at 55°C. 8 g Linalylacetat was immediately poured into the above oil phase. 200 g water solution of 0.8 g cationic surfactant CTAC (2.0% of oil phase) was heated at around 55°C. The oil phase was mixed with the water phase using an Ultrasonic stab (200 w, 13 mm) for 2 min. The pH of the emulsion was adjusted with 2 mL 0.1M NH_4OH from approx. 3.7 to 6.0. The final emulsion was transferred to 500 mL beaker equipped with magnetic stirrer (350 rpm). The emulsion was stirred at 40°C for 12 h for the aging of the shell.

The particle size distribution (PSD) was measured by Bluewave (Microtrac S3500 Bluewave, Microtrac) and the results were: $d_{50} = 0.8 \mu\text{m}$.

The core-shell structure was recognized with the TEM measurements.

5 Example 5:

Lysmereal® of BASF SE (CASNo: 80-54-6) in Luwax V:

5 g of a commercial polyvinylether wax (Luwax V of BASF SE) was dissolved into 5 g PTES and 20 g TEOS solution at 60°C. 5 g Lysmereal was immediately poured into the above oil phase. 200 g water solution of 0.8 g cationic surfactant CTAC (2.0% of oil phase) was heated at around 60°C. The oil phase was mixed with the water phase using an Ultrasonic stab (200 w, 13 mm) for 2 min. The pH of the emulsion was adjusted with 2 mL 0.1M NH_4OH from approx. 3.6 to 6.0. The final emulsion was transferred to 500 mL beaker equipped with magnetic stirrer (350 rpm). The emulsion was stirred at 40°C for 10 h to age the shell.

15 The particle size distribution (PSD) was measured by Bluewave (Microtrac S3500 Bluewave, Microtrac) and the results were: $d_{50} = 0.4 \mu\text{m}$.

The core-shell structure was recognized with the TEM measurements.

Example 6:

20 Lysmereal® of BASF SE (CASNo: 80-54-6) in Paraffin wax:

5 g of a commercial Paraffin wax (Fa. Aldrich, CAS 8002-74-2) was dissolved into 5 g PTES and 20 g TEOS solution at 55°C. 5 g Lysmereal was immediately poured into the above oil phase. 200 g water solution of 0.8 g cationic surfactant CTAC (2.0% of oil phase) was heated at around 55°C. The oil phase was mixed with the water phase using an Ultrasonic stab (200 w, 13 mm) for 2 min. The pH of the emulsion was adjusted with 2 mL 0.1M NH_4OH from approx. 3.6 to 6.0. The final emulsion was transferred to 500 mL beaker equipped with magnetic stirrer (350 rpm). The emulsion was stirred at 40°C for 10 h to age the shell.

25 The particle size distribution (PSD) was measured by Bluewave (Microtrac S3500 Bluewave, Microtrac) and the results were: $d_{50} = 0.4 \mu\text{m}$.

The theoretical loading of Lysmereal is approx. 28%. The loading of the Lysmereal was determined by TGA Measurement. The weight difference of the spray dried sample between 130°C and 300°C is approx. 17%. It means that the loading of the encapsulated Lysmereal should be at least 17%.

What is claimed is:

1. Microcapsules having a core material encapsulated within a microcapsular shell, said core material comprises at least one active ingredient selected from the group consisting of fragrance, perfume and flavour, and wherein the microcapsular shell comprises at least one inorganic/hybrid material obtained by in-situ sol-gel polymerization of said precursors; wherein the concentration of the core material based on total weight of the microcapsules is less than 80 weight-%.
2. Microcapsules according to claim 1, wherein the core material comprises at least one active ingredient selected from the group consisting of fragrance, perfume or flavour and hydrophobic material.
3. Microcapsules according to claim 2, wherein hydrophobic material is selected from the group consisting of wax, vegetable oil, mineral oil or mixtures thereof.
4. Microcapsules according to any one of claims 1 to 3, wherein the microcapsular shell is based on at least one inorganic (semi)metal oxide material.
5. Microcapsules according to claim 4, wherein the inorganic (semi)metal oxide is SiO_2 , ZnO , Al_2O_3 or TiO_2 .
6. Microcapsules according to claim 5, wherein the inorganic (semi)metal oxide is SiO_2 .
7. Microcapsules according to anyone of claims 1 to 6, wherein the active ingredient is selected from the group consisting of hydrophobic fragrance, perfume and flavour.
8. Microcapsules according to any one of claims 1 to 7, wherein the concentration of the core material based on the total weight of the microcapsules is less than 60 weight-%.
9. Microcapsules according to claim 8, wherein the concentration of the core material based on the total weight of the microcapsules is less than 50 weight-%.
10. Microcapsules according to claim 9, wherein the concentration of the core material based on the total weight of the microcapsules is within the range of 10 to 49 weight-%.
11. Microcapsules according to any one of claims 1 to 10, wherein said core material is a liquid core.
12. Microcapsules according to any one of claims 1 to 10, wherein said core material is a liquid oily core.

13. Microcapsules according to any one of claims 1 to 10, wherein said core is a solution, suspension or dispersion.
14. Microcapsules according to claim 1, wherein the precursors are selected from silicon alkoxides monomers, silicon ester monomers and monomers of the formula $\text{Si}(\text{R}_1)_n(\text{R}_2)_m$, wherein R_1 is a hydrolysable substituent, n is an integer from 2 to 4, R_2 is a non polymerizable substituent and m is an integer from 0 to 4, a partially hydrolyzed and partially condensed polymer thereof, and mixtures thereof.
15. Microcapsules according to claim 14, wherein the precursors are mixtures of $\text{SiR}_3(\text{OR}_4)_3$ and $\text{Si}(\text{OR}_5)_4$, wherein R_3 , R_4 and R_5 is independently from one another C_1 - C_6 alkyl.
16. Microcapsules according to claim 15, wherein the precursors are selected from the mixture of the compounds methyltrimethoxysilane (MTMS) and tetraethoxysilane (TEOS), methyltriethoxysilane (MTES) and tetraethoxysilane (TEOS), methyltrimethoxysilane (MTMS) and tetramethoxysilane (TMOS), methyltriethoxysilane (MTES) and tetramethoxysilane (TMOS), *n*-propyltriethoxysilane (*n*-PTES) and tetramethoxysilane (TMOS), *n*-propyltriethoxysilane (*n*-PTES) and tetraethoxysilane (TEOS).
17. Microcapsules according to any one of claims 1 to 16, wherein the fragrance, perfume or flavour contains an emulsifier.
18. Microcapsules according claim 1, wherein the particle size of the microcapsules is less than 100 μm , preferably less than 50 μm .
19. Microcapsules according claim 18, wherein the particle size of the microcapsules is less than 10 μm , preferably less than 2 μm .
20. Microcapsules according to claim 3, wherein the waxes are animal waxes, vegetable waxes, mineral waxes, petroleum waxes or synthetic waxes, or mixtures thereof.
21. Microcapsules according to any one of claims 1 to 20, wherein the fragrance, perfume and flavour is selected from the group consisting of 7-acetyl-1,2,3,4,5,6,7,8-octahydro-1,1,6,7-tetramethyl-naphthalene, .alpha.-ionone, .beta.-ionone, .gamma.-ionone .alpha.-isomethylionone, methylcedrylone, methyl dihydrojasmonate, methyl 1,6,10-trimethyl-2,5,9-cyclododecatrien-1-yl ketone, 7-acetyl-1,1,3,4,4,6-hexamethyltetralin, 4-acetyl-6-tert-butyl-1,1-dimethylindane, hydroxyphenylbutanone, benzophenone, methyl .beta.-naphthyl ketone, 6-acetyl-1,1,2,3,3,5-hexamethylindane, 5-acetyl-3-isopropyl-1,1,2,6-tetramethylindane, 1-dodecanal, 4-(4-hydroxy-4-methylpentyl)-3-cyclohexene-1-carboxaldehyde, 7-hydroxy-3,7-dimethyloctanal, 10-undecen-1-al, isohexenylcyclohexylcarboxaldehyde, formyltricyclodecane, condensation products of hydroxycitronellal and methyl anthranilate, condensation products of

hydroxycitronellal and indole, condensation products of phenylacetaldehyde and indole, 2-methyl-3-(para-tert-butylphenyl)propionaldehyde, ethylvanillin, heliotropin, hexylcinnamaldehyde, amylcinnamaldehyde, 2-methyl-2-(isopropylphenyl)propionaldehyde, coumarin, .gamma.-decalactone, cyclopentadecanolide, 16-hydroxy-9-hexadecenoic acid lactone, 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl-cyclopenta-.gamma.-2-benzopyran, .beta.-naphthol methyl ether, ambroxane, dodecahydro-3a,6,6,9a-tetramethylnaphtho[2,1b]furan, cedrol, 5-(2,2,3-trimethylcyclopent-3-enyl)-3-methylpentan-2-ol, 2-ethyl-4-(2,2,3-trimethyl-3-cyclopenten-1-yl)-2-buten-1-ol, caryophyllene alcohol, tricyclodecenyl propionate, tricyclodecenyl acetate, benzyl salicylate, cedryl acetate, and tert-butylcyclohexyl acetate.

22. Microcapsules according to claim 21, wherein the fragrance, perfume and flavour is selected from the group consisting of hexylcinnamaldehyde, 2-methyl-3 (tert-butylphenyl)-propionaldehyde, 7-acetyl-1,2,3,4,5,6,7,8-octahydro-1,1,6,7-tetramethylnaphthalene, benzyl salicylate, 7-acetyl-1,1,3,4,4,6-hexamethyltetralin, para-tert-butylcyclohexyl acetate, methyl dihydrojasmonate, .beta.-naphthol methyl ether, methyl .beta.-naphthyl ketone, 2-methyl-2-(para-iso-propylphenyl)propionaldehyde, 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-.gamma.-2-benzopyran, dodecahydro-3a, 6,6,9a-tetramethylnaphtho[2,1b]furan, anisaldehyde, coumarin, cedrol, vanillin, cyclopentadecanolide, tricyclodecenyl acetate and tricyclodecenyl propionates.

23. A process for preparing microcapsules having a core material encapsulated within a microcapsular shell, said core material comprises at least one active ingredient selected from the group consisting of fragrance, perfume and flavour, wherein the concentration of the core material based on total weight of the microcapsules is less than 80 weight-%.

said process comprises the step of

(a) preparing a mixture of at least one sol-gel precursor and at least one fragrance, perfume and/or flavour;

(b) preparing an oil-in-water emulsion by emulsification of an oily phase that comprises the core material, in an aqueous phase, under high shear forces, wherein the oily phase comprises at least one sol-gel precursor;

(c) applying conditions for the sol-gel process to obtain nano- or micro-capsules having a metal oxide or inorganic-organic hybrid shell encapsulating the core material, and

(d) optionally introducing external cationic materials to modify the surface of the shell, in order to improve the deposition of microcapsules on the surface.

24. A process according to claim 23, wherein step (a) is defined as

preparing a mixture of hydrophobic material at a certain temperature, at least one sol-gel precursor and at least one fragrance, perfume and/or flavour.

25. A process according to claim 23, wherein the aqueous phase includes a surfactant.

26. A process according to claim 25, wherein the surfactant is a cationic surfactant, especially a cationic surfactant of the formula $R'R''R'''R''''N^+X^-$, wherein independently from of another R' , R'' , R''' and R'''' is C_1 - C_{20} alkyl, X is an anion, preferably a halogen anion, especially a chloride anion.

27. A process according to claim 26, wherein said monoalkylquaternary ammonium surfactants are selected from cetyltrimethyl ammonium chloride, cetyltrimethyl ammonium bromide, lauryltrimethylammonium chloride, stearyltrimethylammonium chloride, cetylpyridinium chloride, and mixtures thereof.

28. A process according to claim 23, comprising adding a catalyst in step (c) to accelerate the formation of the microcapsular shell.

29. A process according to claim 28, which comprises adding an acid or a base as catalyst to provide a pH in the range of 1 to 7.

30. A process according to claim 29, which comprises mixing and stirring the emulsion at suitably selected pH in the range of 2 to 6, preferably to obtain a pH of 3 to 5 of the emulsion.

31. A process according to any one of claims 23 to 30, which comprises mixing in step (c) for at least 3 hours, preferably 5 to 20 hours.

32. A process according to any one of claims 23 to 31, which comprises mixing in step (c) at a temperature in the range of 0 to 100°C, preferably in the range of 10 to 60°C.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2011/055553

A. CLASSIFICATION OF SUBJECT MATTER

INV. B01J13/18 A23L1/22 C11D3/50
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B01J A23L C11D

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 03/034979 A2 (SOL GEL TECHNOLOGIES LTD [IL]; LAPIDOT NOA [IL]; MAGDASSI SHLOMO [IL];) 1 May 2003 (2003-05-01) claims 1, 6, 18-19, 24, 109-110, 115, 118-119, 122, 137, page 30, line 11 - line 17 examples 1-6	1-32
X	WO 01/80823 A2 (SOL GEL TECHNOLOGIES LTD [IL]; LAPIDOT NOA [IL]; MAGDASSI SHLOMO [IL];) 1 November 2001 (2001-11-01) claims 1, 10-11, 30, 44, 55 page 21 examples 1-5	1-32
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Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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Date of the actual completion of the international search

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Name and mailing address of the ISA/

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2011/055553

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2002/064541 A1 (LAPIDOT NOA [IL] ET AL) 30 May 2002 (2002-05-30) claims 1, 6, 18-19, 24, 109-110, 115, 118, 137 paragraph [0168] figures 1-6 -----	1-32
X,P	EP 2 196 257 A2 (INT FLAVORS & FRAGRANCES INC [US]) 16 June 2010 (2010-06-16) claims 1, 5, 7 example 1 paragraphs [0023], [0024], [0043] -----	1-9, 11-14, 17-19, 23-30,32
A	WO 03/039510 A1 (SOL GEL TECHNOLOGIES LTD [IL]; LAPIDOT NOA [IL]; ROTTMAN CLAUDIO [IL];) 15 May 2003 (2003-05-15) the whole document -----	1-32
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