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(54) Title: PROCESS FOR PRODUCING NANO-CAPSULES CONTAINING A FRAGRANCE

(57) Abstract: The present invention relates to the field of perfumery and in particular to a delivery system, in the form of nano-capsules, and a process for making nano-capsules containing a fragrance. Said delivery system comprises an external polymeric wall encapsulating a perfuming oil. The invention's delivery system is able to protect and release in a controlled manner the oil, so as to prolong over the time the perception of the fragrance of the latter. The invention concerns also the uses in perfumery of said delivery system.

PROCESS FOR PRODUCING NANO-CAPSULES CONTAINING A FRAGRANCE

Technical field

The present invention relates to the field of perfumery. More particularly it provides a delivery system, in the form of nano-capsules, and a process for making nano-capsules containing a fragrance. Said delivery system is able to protect and to release in a controlled manner the fragrance, so as to prolong over the time the perception of said fragrance. The invention concerns also the uses in perfumery of said delivery system.

Prior art

The perfume industry has a particular interest for delivery systems which are capable of improving the stability and prolonging the effect of active ingredients over a certain period of time, for example in order to overcome the problems encountered when using perfuming ingredients which are instable and/or too volatile or have a poor substantivity in application. Therefore, there is a real need in finding new and more effective systems capable of solving the problem of prolonging or improving the stability and the perception of perfuming ingredient.

To the best of our knowledge, none of the delivery systems of the present invention is known from the prior art.

The closest prior art is represented by EP 1135429 that reports a process for carrying out polyaddition reactions in miniemulsion containing pre-polymers and optionally traces of highly hydrophobic compounds or solid particles. The delivery system of the present invention, which is in the form of nano-capsules, differentiates from the prior art nano-capsules by the fact that the inner core is composed of a liquid and volatile oil rather than by a polymeric network or a solid particle. Such a difference is important for the purposes of the invention, as it allows a controlled release of the volatile, and is the direct consequence of limitations imposed to the solubility parameters of the components of the capsules.

The prior art document neither describes, nor suggests, a process wherein is used a miniemulsion that contains a predominant amount of a liquid perfuming oil, which does not participate to the polymerization reaction, so as to obtain nano-particles wherein a polymeric wall encapsulates a liquid core, and does not suggest the specific combinations of oils and pre-polymers as claimed by the present invention.

Moreover, said prior art document does not mention the possibility to use the invention's delivery systems as perfuming ingredients.

Description of the invention

In order to solve the problems aforementioned, a first embodiment of the present invention provides a process for making a delivery system in the form of size-stable capsules having an average particle size comprised between 40 and 1000 nm, said process comprising the steps of:

a) producing a miniemulsion comprising a liquid perfuming oil, a water phase, a first pre-polymer and a second pre-polymer, and wherein the droplet size is comprised between 40 and 1000 nm; and

b) inducing a polymerization reaction between the first and the second pre-polymers by means of a catalyst capable of promoting said reaction, so as to form a polymer;

the liquid perfuming oil having a Hansen solubility parameter, δ, comprised between 17 and 25 $MPa^{1/2}$; and

the polymer having a Hansen solubility parameter, δ, comprised between 20 and 30 $MPa^{1/2}$ with the polar and the hydrogen bonding components, δ_D and δ_H respectively, being comprised between 1 and 15 $MPa^{1/2}$.

In Figure 1, the kinetics of the release of 2,2-dimethyl-6-methylene-1-cyclohexanecarboxylate over time from the capsules of the invention are shown. The bold, dashed horizontal line indicates the odour threshold concentration.

By "size-stable capsules" we mean here capsules that do not modify their size owing to collisions and fusion.

By "miniemulsion" we mean here emulsions which are dispersions of an organic phase in a water phase, and if desired one or more surfactants, and wherein the droplet size is essentially comprised between 40 and 1000 nm. In the present invention,

preferably, the droplet size is comprised between 300 and 1000 nm. Moreover, in general, the capsules obtained by the present invention have an average particle size similar to the one of the droplet size of the miniemulsion.

In general, miniemulsions are obtained according to procedures which belong to the general knowledge of the skilled artisan, see for example K. Landfester, Macromol. Rapid Commun. 2001, 22(12), 896-936. For examples one of said procedures comprises the admixture of the components and then their mixture with high shear homogenizer.

The "Hansen solubility parameter δ" is a well-known and established parameter (see C. M. Hansen in "Hansen Solubility Parameters – A User's Handbook", Bocca Raton 2000). Said solubility parameter measures the polarity of a molecular system and, when squared, it can be used to estimate its cohesive energy density which is linked to the heat of vaporization. Said parameter δ comprises a dispersion component δ_D, a polar component δ_P and a hydrogen bonding component, δ_H, the interrelation of which is expressed by the following formula

$$\delta^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \qquad (I)$$

The solubility parameters can be calculated using the well-known program "Molecular Modeling PRO, ChemSW".

It is important to stress out that the specific ranges for the Hansen solubility parameter of the liquid perfuming oil and of the polymer are important for the purpose of the invention. Indeed we have surprisingly found that if the liquid perfuming oils and the polymer are selected in order to satisfy the above-mentioned criteria, it is possible to obtain capsules wherein the liquid perfuming oils is confined into the inner part of the capsule and not randomly distributed between the surface and the inner part. The fact that the oil is confined into the inner part is important, as only in such a case it is possible to efficiently control the evaporation of the oil and therefore prolong the organoleptic effect of the latter.

By "liquid perfuming oil" we mean here an organic phase that is a liquid at about 20°C. Said liquid perfuming oil has a Hansen solubility parameter δ comprised between 17 and 25 $MPa^{1/2}$. Said liquid perfuming oil can be composed of a single perfuming compound, or of a mixture of several single perfuming compounds, having a Hansen

solubility parameter comprised in the range mentioned above. Furthermore, said liquid perfuming oil must be essentially inert towards the pre-polymers present in the miniemulsion as well as the polymer formed during step b) of the invention's process.

By "perfuming compound" it is meant here a compound, which is of current use in the perfumery industry, i.e. a compound that is used as active ingredient in perfuming preparations or compositions in order to impart a hedonic effect. In other words such a compound, to be considered as being a perfuming one, must be recognized by a person skilled in the art of perfumery 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 compounds present 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 compounds belong to chemical classes as varied as alcohols, aldehydes, ketones, esters, ethers, acetates, nitriles, terpene hydrocarbons, nitrogenous or sulphurous heterocyclic compounds and essential oils, and said perfuming compounds 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.

According to a preferred embodiment of the invention, said oil is composed of a single perfuming compound. Yet, according to another embodiment the Hansen solubility parameter is preferentially comprised between 17 and 21 $MPa^{1/2}$.

Moreover, according to a further particular embodiment of the present invention, the perfuming compounds have between 7 and 20, or even between 8 and 15, carbon atoms.

As non-limiting examples of such perfuming compounds one may cite those that are esters, ethers, enones or ketones, in particular esters or ethers, and in particular the compounds cited here-in-below in Table 1, which reports also the values of the respective solubility parameters and its components.

Table 1 : Specific examples of perfuming compounds suitable for the invention's purposes

Compound	$\delta^{1)}$	$\delta_D{}^{1)}$	$\delta_P{}^{1)}$	$\delta_H{}^{1)}$
Methyl 2,2-dimethyl-6-methylene-1-cyclohexanecarboxylate	17.6	16.3	2.6	6.1
∝-Damascone	17.4	15.9	3.7	5.8
1,2,3,4,4Aβ,5,8,8Aβ-Octahydro-2,2,6,8α-tetramethyl-1α-naphthalenol	18.5	15.4	3.2	9.7
1-(5,5-Dimethyl-1-cyclohexen-1-yl)-4-penten-1-one	18.6	17.4	4.1	3.1
Citral	17.4	15.7	2.9	6.8
Cis-2-methyl-4-propyl-1,3-oxathiane	18.5	17.1	3.5	6.0
Ethyl (E)-2,4-dimethyl-2-pentenoate	18.2	16.0	7.8	3.7
3-(3,3/1,1-Dimethyl-5-indanyl)propanal	19.5	18.7	2.6	5.1
3-Methyl-2-hexenyl acetate	17.4	16.0	2.8	6.3
Ethyl (2E)-2,4,7-decatrienoate	17.7	15.6	6.4	5.2
2-Methyl-3-hexanone oxime	21.5	16.4	5.6	12.8
6,7-Epoxy-3,7-dimethyl-1,3-octadiene	17.1	15.9	4.0	4.8
(2E,6Z)-2,6-Nonadien-1-ol	19.9	16.4	4.4	10.4
(1'R)-3-(2',3'-Dimethyl-2'-cyclopenten-1'-yl)butanenitrile	17.4	15.6	6.0	4.8
Benzyl acetate	18.4	16.4	4.3	7.3

1) in $MPa^{1/2}$

The pre-polymers are two other important components of the miniemulsion. Said pre-polymers should comprise at least two functional groups. The functional groups first and second pre-polymers should be capable of reacting together so as to enable the formation of the polymer. Specific examples, but not limiting, of functional groups for the first pre-polymer are isocyanate, esters or carboxylic acids. Specific examples, but not limiting, of functional groups for the second pre-polymer are OH or amino groups.

According to an embodiment of the invention, said first pre-polymer is a C_{8-20} bis-isocyanate, and the second pre-polymer is a diol selected from the group consisting of C_{2-14} diols, C_{12-16} diphenols, polyethylene- or polypropylene-glycol based diols having form 2 to 30 monomeric units and the diols comprising a polyester fragment containing from 1 to 20 monomeric units, or said second pre-polymer is a diamine selected from the group consisting of C_{2-14} diamines, polyethylene- or polypropylene-amine based or polyethylene- or polypropylene-glycol based diamines having form 2 to 30 monomeric units and choline esters C_{2-20} diacids. According to said embodiment, the liquid oil phase preferably contains small amounts, if not devoid, of alcohols or aldehydes.

Specific, but non-limiting, examples of bis-isocyanate are isophorone diisocyanate (IPDI), hexamethylene diisocyanate (HMDI) or its dimer or trimer, toluene diisocyanate and bis(4-isocyanatocyclohexyl)methane.

Specific, but non-limiting, examples of diol are 1,7-heptane diol, 1,6-hexane diol, glycerol, di-, tri- or tetra-ethylene glycol, PEG-400 or 1000 (polyethylene glycols having a molecular weight around 400 or 1000), neopentylglycol, diols comprising an oligomeric polyadipate fragment, bisphenol A.

Specific, but non-limiting, examples of diamines are 1,12-diaminododecane, Jeffamine® D-2000, ED600 or D400, ethylene dimine, 1,6-diaminohexane and bis(3-aminopropyl)amine (BAPA).

Further examples of second pre-polymers are partially hydrolysed polyvinyl acetate, polyvinyl alcohol, hydroxy propyl cellulose, polyolols, Chitosan or aminated polysaccharides, provided that said compounds have a molecular mass lower than 10000 g/mol.

The pre-polymers are selected so as to provide a polymer having a Hansen solubility parameter and the polar and the hydrogen bonding components as defined

above. According to a preferred embodiment of the invention, said polymer has a Hansen solubility parameter which is preferentially comprised between 20 and 25 $MPa^{1/2}$ and the polar and the hydrogen bonding components, δ_D and δ_H respectively, which are comprised between 1 and 10 $MPa^{1/2}$, or even between 1 and 5 $MPa^{1/2}$.

The miniemulsion can advantageously comprise one or more surfactants. Said surfactants can contribute to the stabilization of the miniemulsion. As a general rule, the surfactants should be inert towards the pre-polymers, the fragrance and the capsules walls. As non-limiting examples one may cite surfactants such as sodium dodecyl sulphate (SDS), N,N,N,N-cetyltrimethylammonium bromide (CTAB), polyvinyl alcohol (PVA), polyvinyl pyrrolidone (PVP) and the ones knowns under the tradename Tween® (origin: ICI, UK), Stepanquat (Stepan Company), Texapon® (Cognis). The amount of surfactant added to the miniemulsion can be comprised between 0.01 and 10%, preferably between 0.1 and 5%, by weight of the emulsion.

Furthermore, the miniemulsion can advantageously comprise one or more highly hydrophobic compound, i.e. compounds having a water solubility of less than $7x10^{-5}$ g/l. As a general rule, the highly hydrophobic compound should be inert towards the pre-polymers, the fragrance and the capsules walls. As non-limiting examples one may cite highly hydrophobic compounds such as hexadecane, silanes, siloxanes, long-chain esters and vegetable oils.

The components of the miniemulsion can be admixed together in various ratios. According to an embodiment of the invention, the liquid perfuming oil may account for between 30 and 95 %, more preferably for between 60 and 90 %, of the total weight of the dry capsules obtained by the invention process.

The molar ratio between the two pre-polymers may vary as a function of the type of pre-polymers, i.e. is bi, tri or poly-functional. Is generally said molar ratio is such that ratio between the total number of functional groups of the two pre-polymers is comprised between 0.9 and 1.1.

As mentioned above, the invention's process involves the use of a catalyst capable of promoting the polymerization of the monomers. Said catalyst can be heat, a base, an acid or a radical initiator, depending on the nature of the reaction between the pre-polymers. In general, heat is a simple and efficient catalyst, and can be furnished simply

by rising the temperature of the miniemulsion, for example between 10 and 80 °C. Furthermore when the polymerization is the result of a reaction of a diisocyanate and a diamine or diol, a base, such as 1,4-diazabicyclo[2.2.2]octane, or a coordination complex, such as dibutyltindilaurate, is also suitable.

Furthermore, it is understood that the polymerization reaction is performed on the miniemulsion, and that said miniemulsion has to be maintained as such for the time needed to carry out the polymerization reaction, either by using miniemulsion sufficiently stable either by maintaining strong a stirring.

A further object of the present invention are the delivery systems obtainable according to the above-described process. Said delivery systems consist of capsules wherein a liquid perfuming oil is encapsulated into a polymeric wall that allow to control the rate of evaporation of the perfuming compound into the surroundings, so as to prolong or improve the perception of the fragrance.

Preferred delivery systems are those obtained according to the particulars embodiments of the above-mentioned process. These comprise in particular the delivery systems wherein the capsules have an average particle size comprised between 500 and 1000 nm and/or have a liquid perfuming oil in the form of a pure perfuming compound such as a perfuming ester or ether or even ketone.

Furthermore, the invention's capsules can be in a dry form or in the form of a water suspension optionally containing a colloidal stabilizer.

As previously mentioned, the invention's delivery systems allow the release of the perfuming oil in the surroundings in a controlled manner. Therefore, said delivery systems are a useful perfuming ingredient which can be advantageously used in all the fields of modern perfumery, such as fine perfumery or functional perfumery, as it enables a controlled release of odoriferous molecules.

Indeed, the invention's delivery systems may be advantageously employed in fine or functional perfumery to achieve a more controlled deposition and/or release, of a perfuming oil. For example, perfuming oil present as such in washing compositions can have little staying-power on a surface and consequently be often eliminated, for example in the rinsing water or upon drying of said surface. This problem can be solved by using an invention's delivery system, for which we have been able to show that it possesses a

surprising stability over storage and staying-power or tenacity on surfaces such as textiles. Therefore, the invention's delivery systems, owing to a good substantivity and a controlled release of perfuming oil, can be incorporated in any application requiring the effect of rapid or prolonged release of a perfuming oil as defined hereinabove and furthermore can impart a fragrance and a freshness to a treated surface which will last well beyond the rinsing and/or drying processes. Suitable surfaces are, in particular, textiles, hard surfaces, hair and skin.

Thus, in perfumery, one of the major advantages of the invention resides in the fact that the invention's delivery systems impart an intense fragrance to the treated surface, produced by a perfuming oil, which would not be detected on said surface over a sufficiently long period if the oil had been used as such, i.e. without an encapsulating wall.

Therefore, a further object of the present invention is the use of said delivery systems as perfuming ingredient. In other words it concerns a method to confer, enhance, improve or modify the odor properties of a perfuming composition or of a perfumed article, which method comprises adding to said composition or article an effective amount of at least one invention's delivery system. By "use of the delivery systems" it has to be understood here also the use of any composition containing the delivery systems and which can be advantageously employed in perfumery industry as active ingredients.

Said compositions, which are in fact perfuming composition that can be advantageously employed, as perfuming ingredient, are also an object of the present invention.

Therefore, another object of the present invention is a perfuming composition comprising:

i) as perfuming ingredient, at least an invention's delivery system as defined above;

ii) at least one ingredient selected from the group consisting of a perfumery carrier and a perfumery base; and

iii) optionally at least one perfumery adjuvant.

By "perfumery carrier" we mean here a material which is practically neutral from a perfumery point of view, i.e. that does not significantly alter the organoleptic properties of perfuming ingredients. Said carrier may be a liquid.

As liquid carrier one may cite, as non-limiting examples, an emulsifying system, i.e. a solvent and a surfactant system, or a solvent commonly used in perfumery. A detailed description of the nature and type of solvents commonly used in perfumery cannot be exhaustive. However, one can cite as non-limiting examples solvents such as dipropyleneglycol, diethyl phthalate, isopropyl myristate, benzyl benzoate, 2-(2-ethoxyethoxy)-1-ethanol or ethyl citrate, which are the most commonly used.

Generally speaking, by "perfumery base" we mean here a composition comprising at least one perfuming co-ingredient.

Moreover, by "perfuming co-ingredient" it is meant here a compound, which is used in perfuming preparation or composition to impart a hedonic effect. 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 base 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 co-ingredients belong to chemical classes as varied as alcohols, aldehydes, ketones, esters, ethers, acetates, nitriles, terpene hydrocarbons, nitrogenous or sulphurous heterocyclic compounds and essential oils, and said perfuming co-ingredients can be of natural or synthetic origin. Many of these co-ingredients are in any case listed in reference texts such as the book by S. Arctander, Perfume and Flavor Chemicals, 1969, Montclair, New Jersey, USA, or its more recent versions, or in other works of a similar nature, as well as in the abundant patent literature in the field of 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.

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

An invention's composition consisting of at least an invention's delivery system and at least one perfumery carrier represents a particular embodiment of the invention as well as a perfuming composition comprising at least an invention's delivery system, at least one perfumery carrier, at least one perfumery base, and optionally at least one perfumery adjuvant.

It is useful to mention here that the possibility to have, in the compositions mentioned above, more than one type of invention's delivery system is important as it enables the perfumers to create new tools for their work.

Furthermore, the invention's delivery systems can also be advantageously used in all the fields of modern perfumery to positively impart or modify the odor of a consumer product into which said capsules are added. Consequently, a perfumed article comprising:

i) as perfuming ingredient, at least an invention's delivery system or an invention's composition; and

ii) a consumer product base,

is also an object of the present invention.

For the sake of clarity, it has to be mentioned that by "consumer product base" we mean here a consumer product which is compatible with perfuming ingredients. In other words, a perfumed article according to the invention comprises the functional formulation, as well as optionally additional benefit agents, corresponding to a consumer product, e.g. a detergent or an air freshener, and an olfactive effective amount of at least one invention's compound.

The nature and type of the constituents of the 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 its general knowledge and according to the nature and the desired effect of said product.

Examples of suitable consumer products include solid or liquid detergents and fabric softeners as well as all the other articles common in perfumery, namely perfumes, colognes or after-shave lotions, perfumed soaps, shower or bath salts, mousses, oils or gels, hygiene products or hair care products such as shampoos, body-care products, deodorants or antiperspirants, air fresheners and also cosmetic preparations. As detergents there are intended applications such as detergent compositions or cleaning products for

washing up or for cleaning various surfaces, e.g. intended for textile, dish or hard-surface treatment, whether they are intended for domestic or industrial use. Other perfumed articles are fabric refreshers, ironing waters, papers, wipes or bleaches.

Some of the above-mentioned consumer product bases may represent an aggressive medium for the invention's compound, so that it may be necessary to protect the latter from premature decomposition, for example by encapsulation.

The proportions in which the delivery systems according to the invention can be incorporated into the various aforementioned articles or compositions vary within a wide range of values. These values are dependent on the nature of the article to be perfumed and on the desired organoleptic effect as well as the nature of the co-ingredients in a given base when the delivery systems according to the invention are mixed with perfuming co-ingredients, solvents or additives commonly used in the art.

For example, in the case of perfuming compositions, typical concentrations are in the order of 0.1 % to 20.0 % by weight, or even more, of the delivery systems of the invention based on the weight of the composition into which they are incorporated. Preferably, said concentration is comprised between 0.1 to 5% by weight. Concentrations lower than these can be used when these capsules are incorporated into perfumed articles.

The invention will now be described in further detail by way of the following examples.

Example 1

Preparation of capsules according to the invention

A) A mixture of 24.51g of isophorone diisocyanate (the first pre-polymer), 81.0g of methyl 2,2-dimethyl-6-methylene-1-cyclohexanecarboxylate, 1.17g of hexadecane and 0.36g of 1,4-diazabicyclo[2.2.2]octane (catalyst) was added to 255.0g of water, containing 0.90g of sodium dodecyl sulfate as surfactant is emulsified using a laboratory homogenizer (APV Gaulin, Model 15MR) by 5 cycles at 400kg/cm^3. A solution of 9.50g of 2,2-dimethyl-1,3-propandiol (neopentyl glycol, the second pre-polymer) and 12.40g of water was added drop-wise to 300.0g of the emulsion while stirring at room temperature. By raising the temperature to 70°C, the reaction was

started. The reaction time was 18 hours. A stable dispersion of polyurethane capsules containing methyl 2,2-dimethyl-6-methylene-1-cyclohexanecarboxylate was obtained. A mean particle size of 326nm (volume statistics) and 189nm (number statistics) was measured using a Coulter LS 230.

B) A mixture of 24.51g of isophorone diisocyanate, 81.0g of ethyl (E)-2,4-dimethyl-2-pentenoate, 1.17g of hexadecane and 0.36g of 1,4-diazabicyclo[2.2.2]octane was added to 255.0g of water, containing 0.90g of sodium dodecyl sulfate as surfactant and emulsified using a laboratory homogenizer (APV Gaulin, Model 15MR) by 5 cycles at 400kg/cm^3. A solution of 9.50g of 2,2-dimethyl-1,3-propandiol (neopentyl glycol) and 12.40g of water was added drop-wise to 300.0g of the emulsion while stirring at room temperature. By raising the temperature to 70°C, the reaction was started. The reaction time was 18 hours. A stable dispersion of polyurethane capsules containing ethyl (E)-2,4-dimethyl-2-pentenoate was obtained. A mean particle size of 480nm (volume statistics) and 159nm (number statistics) was measured using a Coulter LS 230.

C) A mixture of 23.49g of isophorone diisocyanate, 81.0g of ethyl (E)-2,4-dimethyl-2-pentenoate, 1.17g of hexadecane and 0.36g of 1,4-diazabicyclo[2.2.2]octane (catalyst) was added to 255.0g of water, containing 0.90g of sodium dodecyl sulfate as surfactant and emulsified using a laboratory homogenizer (APV Gaulin, Model 15MR) by 5 cycles at 400kg/cm^3. A solution of 10.43g of 1,6-hexanediol and 12.50g of water was added drop-wise to 300.0g of the emulsion while stirring at room temperature. By raising the temperature to 70°C, the reaction was started. The reaction time was 18 hours. A stable dispersion of polyurethane capsules containing ethyl (E)-2,4-dimethyl-2-pentenoate ester was obtained. A mean particle size of 478nm (volume statistics) and 338nm (number statistics) was measured using a Coulter LS 230.

D) The experiment described in part B) was repeated by replacing sodium dodecyl sulfate by the following emulsifiers: 1.62g Lutensol AT50 (BASF), a mixture of 0.36g sodium dodecyl sulfate and 1.64g Tween 80 (FLUKA) or 3.00g Texapon NSO

(Cognis/Impag). All experiments gave stable dispersions of polyurethane capsules containing Methyl 2,2-dimethyl-6-methylene-1-cyclohexanecarboxylate. Results are given in Table 2.

Table 2 : Particle diameter for dispersions using various emulsifiers

Emulsifier (type and amount)	Mean diameter (volume statistics)	Mean diameter (number statistics)
- Sodium dodecyl sulfate (SDS)	326nm	189nm
- Lutensol AT50	348nm	311nm
- SDS/Tween 80	346nm	316nm
- Texapon NSO	295nm	126nm

E) A mixture of 8.17g of isophorone diisocyanate, 27.0g of liquid perfuming oil according to Table 3, 0.39g of hexadecane and 0.12g of 1,4-diazabicyclo[2.2.2]octan (catalyst) was added to 85.0g of water, containing 1.00g of Texapon NSO as surfactant and emulsified using a rod-type ultrasonifier (Labsonic 2000, B. Braun) at 200W for 2 min. A solution of 3.83g of 2,2-dimethyl-1,3-propandiol (neopentyl glycol) and 5.0g of water was added drop-wise to the emulsion while stirring at room temperature. By raising the temperature to 70°C, the reaction was started. The reaction time was 18 hours. All experiments gave stable dispersions of polyurethane capsules containing various perfume components. Results are given in Table 3.

Table 3 : Particle diameter for dispersions using various perfume components

Perfume component	Mean diameter (volume statistics)	Mean diameter (number statistics)
- Methyl 2,2-dimethyl-6-methylene-1-cyclohexanecarboxylate	384nm	283nm
- Citral	397nm	291nm
- α-Damascone	523nm	356nm

F) A mixture of 5.90g of isophorone diisocyanate, 27.0g of methyl 2,2-dimethyl-6-methylene-1-cyclohexanecarboxylate and 0.39g of hexadecane was added to 85.0g of water, containing 0.90g of Texapon NSO or 0.23g of sodium dodecyl sulfate as surfactant and emulsified using a rod-type ultrasonicator (Labsonic 2000, B. Braun) at 200W for 2 min. The temperature was raised to 70°C and a solution of 6.10g of bis-(2-aminopropyl)polypropyleneglycol 130 (Jeffamin D230, FLUKA) and 5.0g of water was added dropwise to the emulsion while stirring at 70°C. The reaction time was 5 hours. Both experiments gave stable dispersions of polyurea capsules containing methyl 2,2-dimethyl-6-methylene-1-cyclohexanecarboxylate. A mean particle size of 300-400nm (volume-based) and approx. 100nm (number-based) was measured using a Coulter LS 230.

Example 2

Measures of the performance of delivery systems according to the invention

The measures were carried out with capsules prepared as described in Example 1.

Softening and drying

The terry towels were soaked for >30 min in 20°C tap water, then centrifuged. The softener (5.80 g) was dispersed in 2 liters tap water (20°C).The suspended terry towel was agitated for 6 minutes in the softener solution and then centrifuged. The terry towel was hanged out for drying at 22°C and 50 °C for 20 hours.

Headspace measurements

After 20 hours drying the towels were suspended in a cylindrical flow cell that has been designed for the volatiles collection under controlled conditions. Nitrogen was used as sweeping gas. This cell has been thermostatted at 22°C and the humidity was adjusted to 40%. 10 liters volumes were sampled in about 50 min. The volatiles have been collected by absorption on Tenax cartridges. The cartridges were then desorbed thermally in a Perkin Elmer Turbomatrix ATD desorber and directly analyzed with Agilent GC/MSD (6890N/5973N).

Performance of capsules of example 1

Figure 1 shows the release kinetics of methyl 2,2-dimethyl-6-methylene-1-cyclohexane-carboxylate from the following samples :

i) a softener base comprising 0.5% of free methyl 2,2-dimethyl-6-methylene-1-cyclohexanecarboxylate (o)

ii) a softener base containing capsules (according to example 1.A) (◊).

The final concentration of methyl 2,2-dimethyl-6-methylene-1-cyclohexanecarboxylate in the softener base has fixed at 0.5% for all experiments. The release kinetics represented in Figure 1 show a strong effect of the polyurethane capsules on the release of methyl 2,2-dimethyl-6-methylene-1-cyclohexanecarboxylate.

Claims

1. A process for making a delivery system in the form of size-stable capsules having an average particle size comprised between 40 and 1000 nm, said process comprising the steps of:

a) producing a miniemulsion comprising a liquid perfuming oil, a water phase, a first pre-polymer and a second pre-polymer, and wherein the droplet size is comprised between 40 and 1000 nm; and

b) inducing a polymerization reaction between the first and the second pre-polymers by means of a catalyst capable of promoting said reaction, so as to form a polymer;

the liquid perfuming oil having a Hansen solubility parameter, δ, comprised between 17 and 25 $MPa^{1/2}$; and

the polymer having a Hansen solubility parameter, δ, comprised between 20 and 30 $MPa^{1/2}$ with the polar and the hydrogen bonding components, δ_D and δ_H respectively, being comprised between 1 and 15 $MPa^{1/2}$.

2. A process according to claim 1, characterized in that droplet size is comprised between 300 and 1000 nm.

3. A process according to claim 1 or 2, characterized in that said liquid perfuming oil has a Hansen solubility parameter comprised between 17 and 21 $MPa^{1/2}$.

4. A process according to any one of claims 1 to 3, characterized in that said liquid perfuming oil is composed of a single perfuming compound.

5. A process according to claim 4, characterized in that said liquid perfuming oil is an ester, ether, enone or ketone.

6. A process according to any one of claims 1 to 5, characterized in that said polymer has Hansen solubility parameter which is comprised between 20 and 25 $MPa^{1/2}$ and the polar and the hydrogen bonding components, δ_D and δ_H respectively, which are comprised between 1 and 10 $MPa^{1/2}$.

7. A process according to any one of claims 1 to 6, characterized in that the first pre-polymer is a C_{8-20} bis-isocyanate.

8. A process according to any one of claims 1 to 7, characterized in that the second pre-polymer is a selected from the group consisting of:

a) C_{2-14} diols, C_{12-16} diphenols, polyethylene- or polypropylene-glycol based diols having form 2 to 30 monomeric units and the diols comprising a polyester fragment containing from 1 to 20 monomeric units, and

b) C_{2-14} diamines, polyethylene- or polypropylene-amine based or polyethylene- or polypropylene-glycol based diamines having form 2 to 30 monomeric units and choline esters C_{2-20} diacids.

9. A process according to any one of claims 1 to 8, characterized in that the miniemulsion further comprise one or more surfactants and optionally one or more compound having a water solubility of less than $7x10^{-5}$ g/l.

10. A delivery system obtainable by a process according to any one of claims 1 to 9.

11. A delivery system according to claim 10, characterized in that the liquid perfuming oil in the form of a pure perfuming compound selected from the group consisting of perfuming esters, ethers and ketones.

12. A delivery system according to claim 10, characterized in that the capsules have an average particle size comprised between 500 and 1000 nm.

13. A delivery system according to claim 10, characterized in that the capsules are in a dry form or in the form of a water suspension optionally containing a colloidal stabilizer.

14. Use of the delivery system according to claim 10 as perfuming ingredient.

15. A perfuming ingredient in the form of a composition comprising

i) as perfuming ingredient, at least one delivery system as defined in claim 10;

ii) at least one ingredient selected from the group consisting of a perfumery carrier and a perfumery base; and

iii) optionally at least one perfumery adjuvant.

16. A perfumed article comprising:

i) at least one delivery system, as defined in claim 10, or a composition as defined in claim 15; and

ii) a consumer product base.

17. A perfumed article according to claim 16, characterized in that the consumer product base is a solid or liquid detergent, a fabric softener, a perfume, a cologne or after-shave lotion, a perfumed soap, a shower or bath salt, mousse, oil or gel, a hygiene product, a hair care product, a shampoo, a body-care product, a deodorant or antiperspirant, an air freshener, a cosmetic preparation, a fabric refresher, an ironing water, a paper, a wipe or a bleach.

FIGURE 1 : Kinetic of release of methyl 2,2-dimethyl-6-methylene-1-cyclohexanecarboxylate