



- (51) **International Patent Classification:**
B01J 13/22 (2006.01) *A61Q 17/04* (2006.01)
- (21) **International Application Number:**
PCT/EP2012/051477
- (22) **International Filing Date:**
30 January 2012 (30.01.2012)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:**
11152797.4 31 January 2011 (31.01.2011) EP
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(81) **Designated States** (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) **Designated States** (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- as to the identity of the inventor (Rule 4.17(i))
- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
- of inventorship (Rule 4.17(iv))

Published:

- with international search report (Art. 21(3))

[Continued on next page]

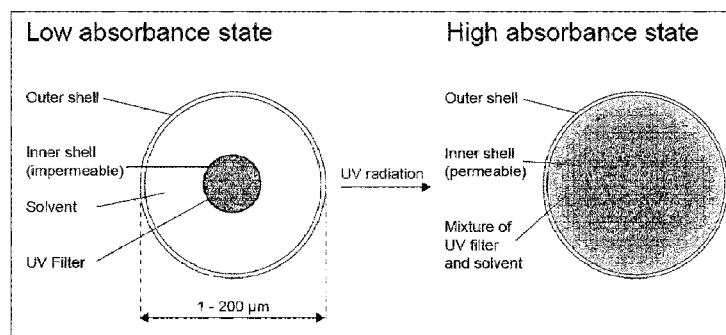
(54) **Title:** PHOTORESPONSIVE MICROCAPSULES AND COMPOSITIONS CONTAINING SAME**Single core microcapsules**

Fig. 3

(57) **Abstract:** The present invention relates to photoresponsive microcapsules comprising one or more first compartment(s) containing at least one sunscreen agent and one or more second compartment(s) containing a solvent or mixture of solvents for said sunscreen agent(s) but containing substantially no sunscreen agent(s) present in the first compartment(s) wherein the border between the first and second compartments becomes at least partially permeable for the sunscreen(s) and/or for the solvent or mixture of solvents upon exposure to an effective amount of UV radiation and/or radiation in the visible spectrum. Further subject matter relates to cosmetic and dermatological compositions containing the inventive microcapsules, methods for the preparation of the microcapsule and the compositions as well as to cosmetic and dermatological methods for protecting skin and/or hair against UV radiation using the compositions.



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- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

Photoresponsive microcapsules and compositions containing same

The present invention relates to photoresponsive microcapsules comprising one or more first compartment(s) containing at least one sunscreen agent and one or more second compartment(s) containing a solvent or mixture of solvents for said sunscreen agent(s) but containing substantially no sunscreen agent(s) present in the first compartment(s) wherein the border between the first and second compartments becomes at least partially permeable for the sunscreen(s) and/or for the solvent or mixture of solvents upon exposure to an effective amount of UV radiation and/or radiation in the visible spectrum. Further subject matter relates to cosmetic and dermatological compositions containing the inventive microcapsules, methods for the preparation of the microcapsule and the compositions as well as to cosmetic and dermatological methods for protecting skin and/or hair against UV radiation using the compositions.

25 Overexposure to UV radiation leads to sunburn (erythema) in human skin. An erythema response may be induced by both UVA and UVB. The minimal erythema dose (MED) is defined as the minimal dose of sunlight radiation needed to produce barely perceptible erythema in a given individual.

Human skin is more sensitive to UVB. The dosage of UVA to produce erythema (20-70 J/cm²) is 600-1000 times that required for UVB (20-1000 mJ/cm²). Although the intensity of UVA at noon is typically 10 times that of UVB, the latter is responsible for 98-99% of delayed erythema development (Shaath, *Sunscreens - Regulations and commercial Development*, Third edition, 2005, by Taylor & Francis Group). Human skin exposed to sunlight on earth is particularly sensitive to 307 nm wavelength sunlight radiation (see the effective spectrum shown in Fig. 1). A wavelength of 307 nm is the most efficient for producing erythema (Shaath, *supra*).

40 The sun protection factor (SPF) indicates a factor of protection against sunburn. It is commonly defined, for a given sun intensity, as the ratio (Q) of the threshold time of developing erythema (an indication of beginning sunburn) on a skin onto which a sunscreen

composition has been applied to the threshold time of developing erythema without application of the sunscreen composition (Pschyrembel/Hunnius Medical and Pharmaceutical Dictionary, Walter de Gruyter 2010). For example, if under a given sun intensity it normally takes one 30 minutes to sunburn, then a sunscreen with SPF 10 will theoretically allow one to stay 10 times longer in the sun (or 300 minutes) before developing sunburn (Department of Health and Human Services FDA, USA. Sunscreen drug products for over the counter use: proposed safety, effectiveness and labelling conditions. Federal Register 1978; 43:38206-69).

A major limitation common to most known sunscreen formulations is that they provide only static protection against UV radiation and do not address the problem that sun intensity varies greatly with numerous factors including time of day, season, latitude, cloud cover, ozone layer thickness, and altitude. Therefore, the static sun protection offered by sunscreen agents in practice provides either underprotection or overprotection.

This static protection results in two types of performance deficits. At high sun intensity, static sunscreen agents underprotect the user. This is expected to result in the biological effects of increased skin aging, and simultaneously, increased DNA mutation rates, leading to skin cancer. At low sun intensity, static sunscreen agents overprotect the consumer, inhibiting sun tanning. Ideally, sunscreen agents would therefore adapt their protection on the skin to correlate with UV index (an international measure for solar UV radiation intensity). Furthermore, and as described above, while the intensity of UVA radiation remains relatively constant throughout the day, the intensity of UVB radiation varies during the day, typically peaking in intensity at solar noon. Analogously therefore, it would be advantageous if sunscreen protection would adapt its protection to correlate with the changing intensity of UVB radiation.

Several approaches have been described in the art to address this problem. PCT/EP2010/062277 describes *inter alia* microcapsules comprising a sunscreen agent capable of undergoing protonation or deprotonation to form a protonated or deprotonated, respectively, sunscreen agent which absorbs, scatters or reflects more or less UV radiation than said sunscreen agent does before being protonated or deprotonated, respectively, wherein said sunscreen agent is present in said microcapsule substantially in its protonated or deprotonated form that absorbs, scatters or reflects less UV radiation than said sunscreen agent does upon protonation or deprotonation, respectively.

To date, several further classes of photoresponsive microcapsules have been described: amongst them are microcapsules that rupture upon irradiation with light due to the generation of gas triggered by such irradiation and a corresponding increase of internal pressure (US 3,301,439; US 4,898,734; Mathiowitz et al. 1981, J Applied Polymer Science 26: 809-922).

- 5 Further prior art microcapsules degrade upon irradiation with light through de-crosslinking of the polymer shell (Yuan et al. 2005, Langmuir 21: 9374-9380) or decomposition of the polymer shell (Katagiri et al. 2009, Chemistry of Materials 21: 195-197).

- 10 WO-A-2007/051198 discloses photoresponsive microcapsules, produced from photoactivatable prepolymers, which become porous to a solution within them upon exposure to light. Such microcapsules are used for light-activated control release of their contents that include solvents, fragrances, flavourings, certain cosmetics, herbicides, insecticides, defoliants, fungicides and insect repellents. Amongst possible cosmetics that may be encapsulated within such microcapsules are described certain sunscreen agents.

- 15 US 6,348,218 describes a cosmetic composition for releasing an active agent onto a user's skin at a release rate, the release rate being a function of exposure to UV radiation, the composition comprising: a medium adapted to be spread onto the user's skin; a multiplicity of microcapsules dispersed in said medium, said microcapsules containing at least one active
20 agent, and said microcapsules having sufficient strength so that only a minority of the microcapsules rupture during application of the composition onto the user's skin; said release rate being controlled by providing a population of microcapsules with half-life times to deterioration under the influence of the UV radiation which is about 1/2 hour to about 6 hours.

- 25 Another problem faced by all topically-applied sunscreen protection is that once applied, such as to the skin and/or hair, they are subject to progressive physical and chemical removal or degradation. For example, this may occur due to physical abrasion on objects such as clothing, or the sunscreen protection may be at least partially removed or dissolved
30 by moisture, such as by washing, rain, swimming or during other water-based activities. Furthermore, sweat may partially remove or degrade the sunscreen formulation; this problem is even increased if the individual is sweating heavily such as by partaking in rigorous physical activity including sports. Hence, although the protection conferred by a topically-applied sunscreen may be adequate (or overprotect) initially upon its application (such as
35 first thing in the morning), this protection can be reduced progressively during the day by the above factors, including to an extent where at midday there is an inadequate amount of

topically-applied sunscreen remaining, and hence providing inadequate protection from UV radiation.

The most common approach to address this problem is simply to improve or otherwise adapt the physical composition and properties of the topical formulation, such as to increase the adhesion or retention of the formulation to the skin, or the resistance of the formulation to removal by abrasion, water or sweat. The skilled person will be aware of the numerous adaptations and improvements made to the composition of topical formulations in order to achieve such effects. However, while this approach may reduce the rate of removal of the formulation; all such formulations are progressively removed, and hence progressively reduce the protection they provide from UV radiation. The only way to maintain (or increase) the level of protection from UV protection with such formulations is therefore to regularly reapply them.

Furthermore, all known commercial organic sunscreens undergo some degree of photodegradation in sunlight. Therefore, sunscreen photostability is of great concern in the sunscreen industry. Sunscreen compositions are typically mixtures of several sunscreen agents, and instability of individual sunscreen agents is responsible for the overall instability of the sunscreen. However, filter combinations of organic and inorganic sunscreen agents are even more prone to photodegradation. For example, irradiation of oxybenzone and titanium dioxide studied by Serpone et al. resulted in about 70% of the oxybenzone being degraded after 20 min of UV exposure (Serpone et al., Photochem Photobiol Sci 2002; 1:970-981). This was a much faster degradation than was observed in a solution containing oxybenzone alone, where 50% was degraded after 260 min. The report by Serpone et al. concluded that oxybenzone degradation was photocatalyzed by titanium dioxide. These two sunscreen agents are present together in many commercially available sunscreen formulations.

Stabilization strategies for photounstable sunscreen agents include adding in the formulation an acceptor that can "quench" the excited state energy of the unstable sunscreen agent. Numerous such stabilizers have been identified for avobenzene, including diethylhexyl 2,6-naphthalate, octocrylene, and methylbenzylidene camphor.

A second strategy has been the removal of ingredients known to be deleterious to a particular sunscreen agent's photostability. This includes removing ingredients that are known to otherwise improve overall performance or photostability of the sunscreen.

A third strategy to prevent photodegradation is to alter solvent polarity in the cosmetic formulation, since sunscreen agents are greatly affected by solvent conditions. For example, studies have demonstrated a direct relationship between the dielectric constant of the oil phase and photo decay of various avobenzene-containing filter combinations (Shaath, 5 Sunscreens - Regulations and commercial Development, Third Edition, 2005).

A fourth strategy is to physically isolate the unstable sunscreen agent from ingredients known to be deleterious to its photostability. Encapsulation is a method well studied for this purpose with avobenzene (Schwack et al., GIT Lab J 1997; 1:17-20; US-A-6,607,713; US-A- 10 6,468,509).

Ideally, a sunscreen should be 100% photostable, and/or should be resistant to removal or degradation, and herein we describe a novel approach to counteract photodegradation, and/or counteract or compensate for the effects of removal or degradation, of sunscreens 15 through use of a novel photoresponsive microcapsules that in certain embodiments steadily increase the protection against sunlight over time, bestowing on the sunscreen an overall net photostability and/or the property of counteracting or compensating for the effects of removal or degradation. Furthermore, the instant invention provides a novel photoresponsive sunscreen system that is able to adapt to the intensity of UV radiation, such as the intensity 20 of UVB radiation as it changes through the day. For example, in certain embodiments the protection to UV radiation conferred by the sunscreen system containing photoresponsive microcapsules correlates with the intensity of UV radiation to which it is exposed, such as an increase in the protection as the intensity of UV radiation increases.

The above further problem of most prior art sunscreen systems has also been addressed in PCT/EP2010/062277 already mentioned above.

The technical problem underlying the present invention is to provide improved microcapsules containing a sunscreen agent that are capable of creating a dynamic protection against UV 30 radiation when formulated into a cosmetic or dermatological formulation. Additionally, it would be advantageous to have microcapsules that would simultaneously protect the skin from undesired effects of active ingredients of sunscreen formulations on skin and/or hair.

The solution to the above technical problem is provided by the embodiments of the present 35 invention as defined herein and in the claims.

The present invention provides microcapsules creating micro-volumes in a cosmetic or dermatological sunscreen composition where UV filters are concentrated and at the same time to create micro-volumes in a cosmetic or dermatological sunscreen composition where UV filters are excluded.

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In particular, microcapsules according to the invention comprise one or more first compartment(s) containing at least one sunscreen agent and one or more second compartment(s) containing a solvent or mixture of solvents for said sunscreen agent(s) but containing substantially no sunscreen agent(s) present in the first compartment(s) wherein
10 the border between the first and second compartments becomes at least partially permeable for the sunscreen(s) and/or the solvent or mixture of solvents upon exposure to an effective amount of UV radiation and/or radiation in the visible spectrum, i.e. any radiation in the wavelength region of about 280 nm to 800 nm, more preferably about 280 to about 400 nm (UV) and/or about 400 to about 800 nm (visible light). The above range of electromagnetic
15 radiation having wavelengths of about 280 nm to about 800 nm is also denoted as the UVIS or UV/VIS spectrum.

Thus, the present invention provides microcapsules containing at least two compartments: the first type of compartment (first compartment or compartment A) contains a sunscreen
20 agent or a mixture of sunscreen agents, and the second type of compartment (second compartment or compartment B) contains a solvent or mixture of solvents for the sunscreen(s) contained in the first compartment(s). It is to be understood that the second compartment(s) may also contain one or more sunscreen agent(s), but these are different from the sunscreen agent(s) present in the first compartment(s). In fact, the solvent or
25 mixture of solvents present in the second compartment may also be compounds having UV absorbing, reflecting and/or scattering properties, i.e. may be UV filters themselves.

A border, e.g. a polymer membrane, separates both compartments. UV and/or visible light containing radiation such as sunlight exposure directly or indirectly makes the border, e.g.
30 the polymer, at least partially permeable for the sunscreen(s) present in the first compartment(s) and/or the solvent or mixture of solvents present in the second compartment. In certain embodiments, the border, e.g. the polymer membrane, ruptures upon exposure to UV radiation and/or visible light. Therefore, upon exposure of the microcapsule (or a composition containing such microcapsules) to an effective amount of UV
35 radiation and/or visible light the contents of compartment A and compartment B at least partially mix.

As a consequence of the UV radiation- and/or visible light-induced permeability or rupture of the border between the compartments, the contents of compartment A is released from compartment A into compartment B. Thus, the UV filter distribution, with respect to the UV filter(s) present in compartment A, within the microcapsule changes from non-homogeneous (uneven distribution) to substantially homogeneous (substantially even distribution). Preferably, after exposure of the microcapsule to UV and/or visible radiation, the distribution of the sunscreen agent(s) within the microcapsule is homogenous at a concentration of from 1 to 75% by weight, more preferably 5 to 50 % by weight, even more preferably 10 to 40 % by weight, particularly preferred 15 to 30 % by weight of the microcapsule.

Furthermore, the contents of compartment B is released from compartment B into compartment A. The solvent distribution, with respect to the solvent or mixture of solvents present in compartment B, within the microcapsule changes from non-homogeneous (uneven distribution) to substantially homogeneous (substantially even distribution).

Thus, upon UV and/or visible light exposure, the concentration of the UV filter(s) in compartment A decreases and the concentration of the UV filter(s) in compartment B increases (with respect to the UV filters present in compartment(s) A before exposure of the microcapsule to UV/visible radiation), whereas the concentration of solvent in compartment B decreases and the concentration of solvent in compartment A increases (with respect to the solvent or mixture of solvents present in compartment(s) B before exposure of the microcapsule to UV radiation and/or visible light).

The working principle of the microcapsule, e.g. when present in a cosmetic formulation, resides on a distribution effect of the sunscreen agents and can be summarized as follows:

It is well known in the art that the efficiency (strength of UV Protection, or SPF) of cosmetic sunscreen formulations depends on the total amount (percentage) of UV filter used in a given cosmetic formulation. The higher the total percentage of UV filters in a cosmetic formulation, the higher the SPF usually is (Shaath (2005), *supra*).

It is also well known in the art, that the distribution of UV filters within a cosmetic formulation greatly influences the SPF. Highest SPFs can be achieved by homogeneously distributing UV filters within a cosmetic formulation (Shaath (2005), *supra*).

Inhomogeneous distribution, such as aggregation of UV filter particles drastically reduces the SPF. Such aggregations often occur, e.g. with inorganic particulates, such as titanium

dioxide or zinc oxide that form aggregates of multiple particulates and thereby dramatically reduce the SPF of a cosmetic sunscreen formulation.

Photoresponsive microcapsules of the present invention preferably form part of a cosmetic or dermatological sunscreen formulation. Redistribution of UV filters and/or activation of UV filters through solvent effects (see below) within the microcapsules of the present invention strongly influences the SPF of the inventive cosmetic/dermatological sunscreen formulation.

Inhomogeneous distribution, such as precipitation of organic UV filters also drastically reduces the SPF. Such precipitations occur when UV filters become insoluble in its solvent and form insoluble crystals or insoluble aggregates.

Inhomogeneous distribution of UV filters is to be understood as having alternating local concentrations of UV filters within a microcapsule changing between high local concentrations, e.g. aggregates of UV filters, in compartment A and low local concentrations, e.g. areas where UV filters are excluded (compartment B = solvent or mixture of solvents).

It should be understood that alternating local concentrations of UV filters do not change the overall/total concentration of UV filters within a cosmetic formulation.

It is also well known in the art that the SPF rating of a cosmetic formulation is very sensitive to changes in total absorbance. Fig. 2 shows the dependence of the SPF in relation to % of total absorbed UV light. The graph clearly shows that even very small changes in absorbance can cause significant changes in SPF. For example shifting total absorbance from 93% to 96% causes an SPF shift from SPF 15 to SPF 30.

The present invention makes it feasible to create micro-volumes in a cosmetic sunscreen composition where UV filters are concentrated (Compartment A of the microcapsules of the present invention) while at the same time to create micro-volumes in a cosmetic sunscreen composition where UV filters are excluded (Compartment B of the microcapsules according to the present invention).

Light-induced redistribution of UV filters - by release of UV filters from compartment A into compartment B - leads to a more homogeneous distribution of UV filters increasing the SPF of a cosmetic sunscreen composition.

Microcapsules of the present invention may contain one UV filter or mixtures of more than one UV filter. Particularly useful are combinations of a UVA and a UVB filter. For example, the first compartment(s) may contain at least one UVA sunscreen agent and at least one UVB sunscreen agent. In other embodiments, it is preferred that the first compartment(s) contain(s) at least one UVA sunscreen agent and the second compartment(s) contain(s) at least one UVB sunscreen agent. Yet in further preferred embodiments, the first compartment(s) contain(s) at least one UVB sunscreen agent and the second compartment(s) contain(s) at least one UVA sunscreen agent. It is also contemplated to provide microcapsule wherein the first compartment(s) contain(s) at least one organic sunscreen agent and the second compartment(s) contain(s) at least one inorganic sunscreen agent (or vice versa).

The microcapsules according to the present invention, in particular the first compartment(s), may contain UV filters in pure form without solvent or they may be present in solubilised form such as a solution in a suitable solvent.

Thus, according to preferred embodiments of the present invention, the microcapsules, in particular the first compartment(s), may contain UV filters in pure liquid form, or dissolved in a suitable solvent.

In other embodiments, the microcapsules, more preferably the first compartment(s), may contain UV filters in solid form, either crystalline or amorphous, or in suspension.

A particularly embodiment of the invention is a microcapsule containing UV filters in its solid form, either pure or in suspension: upon light-induced opening of compartment A such solid form of UV filter gets into contact with the solvent of compartment B and becomes at least partially solubilized by the solvent of compartment B. This form of the invention is particularly effective, because solid forms of UV filters show very little contribution to the UV protecting effect of a cosmetic sunscreen.

Further preferred embodiments of the invention relate to sunscreen formulations that contain more than one type of microcapsules containing UV filters as defined herein. For example, the present invention provides cosmetic and dermatological compositions containing combinations of microcapsules wherein the border between the first and second compartments is more sensitive to UV and/or visible light-containing radiation such as sunlight (fast responding to sunlight) and microcapsules having a border between the first and second compartment being less sensitive to UV radiation and/or visible light (low

responding microcapsules). Such combinations can successively increase protection over a long period of time.

Further subject matter of the invention relates to sunscreen formulations that contain combinations of UVA absorbing microcapsules and UVB absorbing microcapsules.

Yet further embodiments of the present invention provide sunscreen formulations containing combinations of microcapsules of different sizes (i.e. different average diameter).

The inventive microcapsule is particularly useful in sunscreen formulations for cosmetic applications or in dermatological formulations for medical applications.

Thus, further subject matter of the present invention relates to a cosmetic or dermatological (i.e. pharmaceutical) composition comprising the microcapsules as disclosed herein. In various aspects such a cosmetic composition will also be referred to herein as a "sunscreen formulation" (e.g. embodiments already outlined above).

The terms "sunscreen agent" (or simply "sunscreen") and "UV filter" according to the present invention are used synonymously and embrace all molecules capable of absorbing, scattering or reflecting UV radiation, i.e. radiation in the range of wavelengths from about 290 nm to about 400 nm, in particular for protecting (human or animal) skin or hair against such radiation.

In the context of the present invention "UV radiation" means light that contains at least part of the UV spectrum, in particular a UVB component (wherein "UV" and "UVB" radiation are as defined above). Typical UV-, especially UVB-containing light is sunlight. In certain further embodiments, the radiation that makes the border between the first and second compartment(s) at least partially permeable for the sunscreen(s) and/or the solvent(s) may have less energy than UV radiation such as radiation in the visible spectrum as defined above. Thus "visible light" or "light in the visible spectrum" means light that contains at least part of the spectrum of the electromagnetic spectrum that is visible for humans.

In certain embodiments, the UV radiation and/or the visible light has a spectrum that is generally equivalent to that of sunlight, for example that of natural sunlight or of simulated sunlight such as provided by sunlight simulators, sunlamps or sunbeds. In preferred embodiments, the UV radiation/visible light is comprised in, or is, sunlight, such as natural sunlight or simulated sunlight. The intensity of such radiation (UV and/or visible light) is

sufficient for at least partially removing the separation (border) between the first and second compartment(s), e.g. by employing polymers and additives as described further herein below. Such an intensity of UV radiation and/or visible light, for example sunlight, may be described as an "effective amount" of UV radiation/visible light.

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Thus, the microcapsules of the present invention may also respond to the visible spectrum of sunlight (around 400 to 800 nm) to increase the SPF. In certain preferred embodiments of this aspect of the invention, the UV part of the electromagnetic spectrum has no contribution to the breaking of the border such as a polymer membrane between the first and second compartment(s). Such applications are particularly useful for certain applications, e.g. photostabilizers. In practical terms this would also avoid possible problems with a potential "self protection" of the microcapsules by the UV filter(s) contained therein.

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Sunscreen agents or UV filters for use in the present invention can be classified into two groups according to their nature: inorganic and organic sunscreen agents. Inorganic UV filters, or also so-called physical UV filters, principally work by reflecting and scattering the UV radiation, while the organic UV filters, or also called chemical UV filters, absorb the light.

15

The physical UV filters are generally metallic oxides having an atomic number ranging from about 10 to about 40, although silicates and talc may also been used. Particularly preferred metal oxides are titanium and zinc oxide.

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Physical UV filters provide higher protection than the chemical ones and they are insoluble in water.

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It is well known in the art that combinations of organic and inorganic UV filters provide particularly high SPFs to cosmetic sunscreens. Combinations of organic and inorganic UV filters have synergistic effects providing higher SPFs than using inorganic or organic UV filters separately. Inorganic UV filters scatter and/or reflect UV light thereby increasing the path length of light travelling through a layer of sunscreen. This makes organic UV filters more effective. According to Lambert Beers law does the path length of light travelling through an optical medium correlate with the amount of absorbed light. It is therefore a preferred embodiment of the present invention to provide microcapsules as defined herein containing one or more organic UV filter(s) in compartment(s) A and one or more inorganic UV filter(s) in compartment(s) B. Light induced mixing of organic and inorganic UV filters then increases UV protection.

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Organic sunscreen agents for use in the present invention are, compared to inorganic sunscreens, in general better accepted by costumers. Typically, organic sunscreen agents are substituted aromatic compounds whose absorbance in the UV range depends on photochemical excitation of their conjugated p-electron system.

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In particular embodiments, the sunscreen agent is an organic sunscreen agent selected from the group of those that have been approved for commercial use, for example one approved for use under applicable regulation by the United States Food and Drug Administration (FDA), the European Commission's Scientific Committee on Consumer Products (SCCP) (such as those published by the European Cosmetic Toiletry and Perfumery Association (COLIPA)), the Japanese Ministry of Health, Labour and Welfare (MHW) Medicine Bureau and/or the Australian Therapeutic Goods Administration (TGA). The skilled person will be aware of how to identify whether a particular organic sunscreen agent has been so approved, and currently the following specific organic sunscreen agents (sorted by group)

10 have been so approved:

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Anthranilates: menthyl anthranilate. Benzophenones: benzophenone, benzophenone-1, -2, -3, -4, -5, -6, -8, -9, beta 2-glucopyranoxy propyl hydroxy benzophenone, diethylamino hydroxy benzoyl hexyl benzoate. Benzotriazoles: drometrizole, drometrizole trisiloxane, methylene bis-benzotriazolyl tetramethylbutylphenol. Camphors: 3-benzylidene camphor, benzylidene camphor sulfonic acid, camphor benzalkonium methosulfate, 4-methylbenzylidene camphor, poly acrylamido methyl benzylidene camphor, terephthalylidene dicamphor sulfonic acid. Cinnamates: cinoxate, DEA methoxycinnamate, diisopropyl methyl cinnamate, ethylhexyl methoxycinnamate, ferulic acid, glyceryl ethylhexanoate

20 dimethoxycinnamate, isoamyl p-methoxycinnamate, isopentyl trimethoxycinnamate trisiloxane, isopropyl methoxycinnamate, octocrylene. Dibenzoyl methanes: butyl methoxydibenzoylmethane, dimethoxyphenyl-1-(3,4)-4,4-dimethyl-1,3-pentanedione.

Imidazoles: disodium phenyl dibenzylimidazole tetrasulfonate, ethylhexyl dimethoxy benzylidene dioximidazoline propionate, phenylbenzimidazole sulfonic acid.

30 Malonates: polysilicone-15. Para aminobenzoic acids: ethyl dihydroxypropyl PABA, ethylhexyl dimethyl PABA, glyceryl PABA, PABA, PEG-25 PABA, pentyl dimethyl PABA. Phenols: digalloyl trioleate. Phenyl triazines: bis-ethylhexyloxyphenol ethoxyphenyl triazine. Salicylates: ethylhexyl salicylate, homosalate, isopropylbenzyl salicylate, salicylic acid, TEA salicylate. Triazones: diethylhexyl butamido triazone, ethylhexyl triazone.

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With respect to chemical structures and further examples of useful sunscreen agents in the context of the present invention it is referred to the corresponding sections of

PCT/EP2010/062277 the corresponding disclosure of which is hereby incorporated in its entirety into the present description by reference.

In preferred embodiments of the present invention UV filters commonly used for cosmetic applications are used as sunscreen agents in the inventive microcapsule:

Key – INCI name (INCI = International Nomenclature for Cosmetic Ingredients)

3BC - 3-benzylidene camphor

BCS - Benzylidene camphor sulphonic acid

BDM - Butyl methoxydibenzoylmethane

10 BZ1 - Benzophenone-1

BZ2 - Benzophenone-2

BZ3 - Benzophenone-3

BZ4 - Benzophenone-4

BZ6 - Benzophenone-6

15 BZ8 - Benzophenone-8

BZ9 - Benzophenone-9

CBM - Camphor benzalkonium methosulfate

CX - Cinoxate

DBT - Diethylhexyl butamido triazone

20 DDP - 1-(3,4-Dimethoxyphenyl)-4,4-dimethyl-1,3-pentanedione

DHH Diethylamino hydroxybenzoyl hexyl benzoate

DMC Diisopropyl methyl cinnamate

DRT Drometrizole trisiloxane

EDP Ethylhexyl dimethyl PABA

25 EDDP Ethylhexyl dimethoxybenzylidene dioximidazolidine propionate

EMC - Ethylhexyl methoxycinnamate

EMT - bis-Ethylhexyloxyphenol methoxyphenyl triazine

ES - Ethylhexyl salicylate

ET - Ethylhexyl triazone

30 FA - Ferulic acid

GED - Glyceryl ethylhexanoate dimethoxycinnamate

GPH - 4-(2-beta-Glucopyranosiloxy) propoxy-2-hydroxybenzophenone

HS - Homosalate

IMC - Isoamyl p-methoxycinnamate

35 IPM - Isopropyl methoxycinnamate

ITT - Isopentyl trimethoxycinnamate trisiloxane

MA - Menthyl anthranilate

MBC - 4-Methylbenzylidene camphor

MBT - Methylene bis-benzotriazolyl tetramethylbutylphenol

OCR - Octocrylene

P15 - Polysilicone-15

5 P25 - PEG-25 PABA

PAB - PABA

PBC - Polyacrylamidomethyl benzylidene camphor

PBS - Phenylbenzimidazole sulphonic acid

PDP - Pentyl dimethyl PABA (mixed isomers)

10 PDT - Disodium phenyl dibenzimidazole tetrasulfonate

TDS - Terephthalylidene dicamphor sulphonic acid

TiO₂ - Titanium dioxide

TS - TEA-salicylate

ZnO - Zinc oxide

15

The term "sunscreen agent" according to the present invention also includes polymeric substances. Examples of this type of sunscreen agents useful in the present invention include, but are not limited to, polyaniline, poly(N-vinyl pyrrolidone), poly(styrene-N,N-dimethylaminoethyl methacrylate), poly(vinyl pyrrolidone), polyamide, polyindole, polypyrrole, polystyrene sulfonate, polythiophene, polyurea, polyurethane, polyurethane-polyurea, or copolymers containing these polymers.

20

It is clear from the foregoing that the photoresponsive microcapsules of the invention preferably have a lower UV absorbance state before being exposed to UV radiation and/or visible light and switch to a higher UV absorbance state after being exposed to UV radiation and/or visible light.

25

The low UV absorbance state of the photoresponsive microcapsules is characterized by a compartmentation where at least one UV filter is located within one compartment (first compartment or compartment A) and a solvent or mixture of solvents (for the at least one UV filter present in the first compartment) is located within another compartment (second compartment or compartment B).

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The high absorbance state of the photoresponsive microcapsules is characterised by non-compartmentation, where the at least one UV filter and the solvent or mixture of solvents are mixed forming, for example, a suspension or solution.

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The low absorbance state of the photoresponsive microcapsules is further characterized in that an impermeable border such as a membrane, e.g. a polymer membrane, separates UV filter(s) and solvent(s).

- 5 The high absorbance state of the photoresponsive microcapsules is further characterized in that the border between first and second compartment(s) becomes at least partially permeable for the UV filter(s) and/or the solvent(s) such that UV filter(s) and solvent(s), which were separated before, can mix.
- 10 Microcapsules of the present invention may have different structures. Preferred examples are a single core structure (Fig. 3), multi core structure (Fig. 4) or multiple shell (or layer) structure (Fig. 5). Thus, microcapsules of the present invention may comprise an outer polymer shell and having one (single core structure) or more (either in the form of a multiple shell structure or a multi core structure) first compartment(s) having an inner polymer shell
- 15 within the microcapsule. In microcapsules having a multi core structure the multiple cores (i.e. the first compartments or compartments A) may have equal or different sizes. It is to be understood that the structures such as those shown in Figs. 3 to 5 are only exemplary and other possible structures are contemplated (for example, a substantially spherical microcapsule wherein one half-sphere represents compartment A and the other half-sphere
- 20 represents compartment B).

The term "solvent" used in the present invention relates to all compounds in which the sunscreen agents useful in the present invention can be dissolved or suspended and includes organic, aqueous or silicon based solvents.

- 25 Solvents used in the context of the present invention are preferably selected where sunscreens show A) excellent solubility, B) optimal $\lambda_{\max}$, and C) high extinction coefficients. Since most of the UV filters used in the present invention respond differently to solvent polarity, solvent pH, hydrogen bonding ability etc., solvents have to be individually selected and optimized for each individual UV filter or combination of UV filters. The following general
- 30 guidelines are generally considered by the skilled person:

pH effects on UV filters (see Shaath (2005), *supra*, and references cited therein):

- The UV absorption spectra of acidic and basic UV filters may be affected by pH. In acidic UV
- 35 filters, the use of alkaline conditions (pH > 9) will assist in the formation of anions that tend to increase delocalization of electrons. This electron delocalization would decrease the energy required for the electronic transition in the UV spectrum; hence, a bathochromic shift is

observed (longer wavelength or λ_{max}). For example, phenols in an alkaline environment will experience this anticipated bathochromic shift owing to the formation of the phenolate anion. This phenolate anion will participate in resonance delocalization of electrons. Acidic conditions ($\text{pH} < 4$) will assist in the formation of cations with aromatic amines. A hypsochromic shift towards the lower wavelength occurs because the protonation of the unbound lone pair of electrons with acid would prevent any resonance delocalization of the electrons. Thus padimate O, for example, forms the padimate O cation at low pH and a considerable hypsochromic shift occurs with loss of UV protection. Thus, UV filters such as PABA, Padimate O, sulisobenzene, or Uvinul A experience absorbance changes depending on the solvent pH. To achieve maximal protection, the pH of the solvent of compartment B has to be optimized and individually selected for maximal/optimal protection.

Effect of emollients on the efficacy of UV filters: (see Shaath (2005), *supra*, and references cited therein):

Solvent shifts in sunscreen chemicals due to their combinations with a variety of emollients have been observed. The use of different emollients in sunscreen formulations may profoundly influence the effectiveness of a sunscreen chemical. The shifts in the UV spectrum are due to the relative degrees of solvation by the emollient in the ground state and the excited state of the chemical. To predict the effect the emollient has on a particular chemical, the interaction (mostly hydrogen bonding) between the emollient and the sunscreen chemical must be understood. The solvation of polar sunscreens (e.g., PABA) with polar solvents such as water or ethanol will be quite extensive. This extensive solvation stabilizes the ground state, thereby inhibiting electron delocalization. The net result would be a hypsochromic shift to lower wavelengths.

For less polar sunscreen compounds, such as padimate-O, the solvent-solute interaction (hydrogen bonding) is different because the excited state is more polar than the ground state. The net result is stabilization of the excited state by polar solvents. This then lowers the energy requirements for the electronic transition; hence, a higher λ_{max} would be expected, and a bathochromic shift occurs. For sunscreen compounds such as salicylates and anthranilates, they are subject to the "ortho" effect, which supersedes other resonance delocalization effects for the observed UV transitions. The six-membered ring formation reduces the energy requirements for the electronic transition in the molecule by loosening the electrons in the carbonyl group that is conjugated to the aromatic ring.

This lower-energy transition is reflected in a higher than usual λ_{max} . Most of the available electrons are involved in the six-member cyclic arrangement and are not available for

interaction with the solvent molecules. Thus, salicylates and anthranilates usually do not exhibit significant solvent shifts.

Solvents that shift the absorbance spectra and/or shift the λ_{max} and/or decrease the extinction coefficient of a particular UV filter in a way that the UV filter absorbs, scatters or reflects less UV radiation are considered “deactivating” solvents. Analogously, solvents that shift the absorbance spectra and/or shift the λ_{max} and/or decrease the extinction coefficient of a particular UV filter in a way that the UV filter absorbs, scatters or reflects more UV radiation are considered “activating” solvents.

In the context of the present invention particularly useful combinations of solvents use “deactivating” solvents in compartment A and/or “activating” solvents in compartment B. In the context of the current invention this is referred to the “solvent effect” (as compared to the “distribution effect” described above).

In the context of the present invention, solvents may have the form of, e.g. hydrophilic or hydrophobic liquids, crosslinked or non-crosslinked polymer gels, hydrogels, oils, waxes.

Preferred examples of solvents useful in the present invention include those groups of solvents/emollients and specific examples as listed in the following Table 1 which are frequently found in cosmetic formulations. In this context, it is to be understood that emollients such as those in the following table may also be used as “solvents” in the inventive microcapsules and/or cosmetic or dermatological compositions containing such microcapsules. As a rule, such emollients (due to their viscosity) provide for a comparatively slow mixing between the contents of compartment A and the contents of compartment B after exposure of the microcapsule to UV radiation and/or visible light.

Tab. 1: Solvents/Emollients especially useful in the present invention

Group of solvents/emollients	Examples
Esters of polyvalent alcohols without free hydroxyl groups	C18–36 Acid Glycol Ester C18–36 Acid Triglyceride Caprylic/Capric/Linoleic Triglyceride Caprylic/Capric/Stearic Triglyceride Caprylic/Capric Triglyceride Caprylyl Glycol Cocoglycerides

	C10–18 Triglyceride Dicocoyl Pentaerythrityl Distearyl Citrate Glycol Distearate Pentaerythrityl Tetracocoate Pentaerythrityl Tetraoctanoate Pentaerythrityl Tetraoleate Propylene Glycol Dicaprate Propylene Glycol Dicaprylate/Dicaprate Propylene Glycol Dioctanoate Propylene Glycol Dipelargonate Triarachidin Tribehenin Triheptanoin Trihydroxymethoxystearin Trihydroxystearin Triisostearin Trilaurin Trilinolein Trilinolenin Triolein Tripalmitin Tristearin
Waxes and wax-like emollients	Acetylated Lanolin Acetylated Lanolin Alcohol Arachidyl Propionate Behenyl Beeswax C12–15 Alkyl Benzoate C20–40 Alkyl Stearate Cetearyl Heptanoate Cetearyl Isononanoate Cetearyl Octanoate Cetearyl Palmitate Cetyl Acetate Cetyl Esters Cetyl Laurate Cetyl Octanoate Cetyl Palmitate

	Cetyl Ricinoleate Coco-Caprylate/Caprate Decyl Oleate Dibutyl Adipate Di-C12–13 Alkyl Malate Dioctyl Succinat Ethyl Linoleate Hexyldecyl Laurate Hexyl Laurate
Wax esters	Isodecyl Laurate Isononyl Isononanoate Isopropyl Isostearate Isopropyl Lanolate Isopropyl Myristate Isopropyl Palmitate Isopropyl Stearate Isotridecyl Myristate Myristyl Myristate Octyldodecyl Myristate Octyl Octanoate Octyl Palmitate Octyl Stearate Oleyl Erucate Oleyl Oleate Stearyl Caprylate Stearyl Heptanoate Stearyl Octanoate
Alcohols/Fatty acids	Batyl Alcohol (Batilol) Octyldodecanol Palm Kernel Acid
Silicones, Polysiloxanes	Bisphenylhexamethicone Cetyl Dimethicone Cyclomethicone Dimethicone Dimethicone Copolyol Dimethicone Copolyol Stearate Methicone

	Phenyl Dimethicone Phenyl Trimethicone Simethicone Stearyl Dimethicone Trimethylsiloxysilicate
Saturated and unsaturated carbohydrates	Cera Microcristallina Ceresin C13–14 Isoparaffin Dioctylcyclohexane Isohexadecane Ozokerit Paraffin Paraffinum Liquidum Petrolatum Polybutene Polyethylene Polyisoprene Squalene
PEG-Alkylethers o. Alkylesters	Avocado Oil PEG-11 Esters Hydrogenated Palm/Palm Kernel Oil PEG-6 Ester
Hydrophilic solvents	Butylene Glycol Dipropylene Glycol Ethanol Ethoxydiglycol Ethylacetat Glycerin Isopropyl Alcohol PEG-4, 6, 8, 12, 32, 75, 90, 150 PPG-2 Methyl Ether PPG-3 Methyl Ether Propylene Carbonate Propylene Glycol Triethylene Glycol Turpentine

With respect to solvents for use in the present invention it is to be understood that the “solvent” (or mixture thereof) present in the second compartment may have itself have UV

absorbing, reflecting and/or scattering properties such that it may serve itself as a “sunscreen agent” or “UV filter” in the second compartment(s).

Additional ingredients useful in the present invention to solubilise UV filters (either within the inventive microcapsule or additional sunscreen agents which may be optionally present in compositions according to the invention) include gel formers, thickeners and emulsifiers which each may be selected from the groups and specific examples according to Tables 2 to 4:

10 Tab. 2: Examples of gel formers useful in the context of the invention

Group of gel formers	Specific Example
Organic native gel formers	Gelatine Hydrolyzed Collagen Alginic Acid Carrageenan Hyaluronic acid Microcrystalline Cellulose Natriumalginat Pectin Astragalus gummifer Xanthan Gum Solanum tuberosum Zea mays Oryza sativa Triticum vulgare
Organic and semisynthetic gel formers	Cellulose gum Cetyl Hydroxyethylcellulose Ethylcellulose Hydroxyethylcellulose Hydroxypropylcellulose Hydroxypropyl Methylcellulose Methylcellulose Methyl Hydroxyethylcellulose Desamido Collagen Dextran Sulfate Dextrin

	Hydroxypropyl Guar Propylen Glycol Alginate Sodium Carboxymethyl Betaglukan
Synthetic gel formers	Acrylates/C10–30 Alkyl-Acrylate Crosspolymer Acrylates Copolymer Sodium Polyacrylate Polyacrylsäure Polyacrylicacid Glyceryl Polyacrylate Sodium Carbomer Sodium Polymethacrylate Polyacrylamide PVP PVP/Eicosene Copolymer PVP/Hexadecene Copolymer PVP/VA Copolymer Tricontanyl PVP Methoxy PEG-22/Dodecyl-Glycol Copolymer Polybutene Polyethylene Polyquaternium div. No. Polyvinyl Acetat Polyvinyl Alcohol PVM/MA Copolymer PVM/MA Decadiene Crosspolymer Stearalkonium Hectorite Vinylcaprolactam/PVP/Dimethyl- aminoethyl Methacrylate Copolymer
Inorganic gel formers	Bentonite Hectorite Silica Hydrated Silica Montmorillonite Magnesium Aluminium Silikat

Tab. 3: Examples of thickeners (viscosity increasing compounds) useful in the context of the invention

Thickeners	Aluminium/Magnesium Hydroxid, Stearat Magnesium Stearate Zinc Ricinoleate Alumina Ammonium Chloride Magnesium Sulfate Potassium Chloride Sodium Chloride Macrogol-120 Methylglucosediolate Cera alba Candelilla cera Carnauba Cetyl palmitate Theobroma cacao Elaeis guineensis Hydrogenated Castor Oil Butyrospermum parkii
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Tab. 4: Examples of emulsifiers useful in the context of the invention

Group of emulsifiers	Specific example
Anionic emulsifiers	Potassium Cocoate Potassium Oleate Potassium Olivat Potassium Peanutate Potassium Stearate Sodium Oleate Sodium Olivat Sodium Palmate Sodium Palmitate Sodium Ricinoleate Sodium Stearate Sodium Tallowate

	Potassium Lauryl Sulfate Sodium Cetearyl sulfate Sodium Myreth Sulfate Sodium Trideceth Sulfate Cetyl Phosphate Potassium Cetyl Phosphate Gummi arabicum
Amphotheric emulsifiers	Hydrogenated Lecithin Lecithin Phosphatidylcholin
Neutral emulsifiers	DEA-Cetyl Phosphate Dicetyl Phosphate Dimyristyl Phosphate Oleth-3 Phosphate Lauric Acid Myristic Acid Stearic Acid Glyceryl Behenate Glyceryl Caprate Glyceryl Caprylate Glyceryl Cocoate Glyceryl Hydroxystearate Glyceryl Isostearate Glyceryl Lanolate Glyceryl Laurate Glyceryl Linoleate Glyceryl Linolenate Glyceryl Oleate Glyceryl Ricinoleate Glyceryl Myristate Glyceryl Stearate Hydrogenated Tallow Glyceride Octoxyglyceryl Behenate Octoxyglyceryl Palmitate Propyleneglycol Stearate SE Propylene Glycol Stearate Polyglyceryl-3 Diisostearate

	Polyglyceryl-4 Isostearate Polyglyceryl Methyl Glucose Distearate Polyglyceryl-3 Oleate Polyglyceryl-3 Ricinoleate PEG-6 Caprylic/Capric Glycerides PEG-60 Evening Primrose Glycerides PEG-7, 30 Glyceryl Cocoate PEG-15 Glyceryl Isostearate PEG-12 Glyceryl Laurate PEG-75 Glyceryl Pelargonate PEG-20 Glyceryl Ricinoleate PEG- 5, 8, 30 Glyceryl Stearate PEG-20 Glyceryl Stearate PEG-200 Glyceryl Tallowate PEG-20 Methyl Glucose Sesquistearate PEG-10 Olive Glycerides PEG-3/PPG-2 Glyceryl/Sorbitol/Hydroxystearate/ Isostearate Ceteareth-3, 6, 12, 15, 20, 25, 30, 33 Ceteth-16 Choleth-24 Coceth-20 C12-13 Pareth-3, 7 Hydrogenated Talloweth-60 Myristyl Glycol Isosteareth-10 Stearate Isosteareth-2 Laureth-2, 3, 4, 5, 6, 7, 10 Laureth-8, 9, 11, 12, 13 Myreth-4 Myreth-3 Myristate Oleth-10, 15, PPG-2 Ceteareth-9 PPG-5 Ceteth-20 PPG-25 Laureth-25 PPG-1 PEG-9 Lauryl Glycol Ether Steareth-2, 10, 20, 21, 25 Steareth-7
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	Trideceth-7, 9
	Trideceth-12
	C12-20 Acid PEG-8 Ester
	Olive Oil PEG-10 Ester
	PEG-8 Beeswax
	PEG-7, 35, 36 Castor Oil
	PEG-40 Castor Oil
	PEG-10 Cocoate
	PEG-4, 8 Dilaurate
	PEG-3, 8 Distearate
	PEG-2, 7, 20, 25, 40 Hydrogenated Castor Oil
	PEG-20 Hydrogenated Palm Oil Glycerides
	PEG-15 Hydroxystearate
	PEG-26 Jojoba Acid
	PEG-5 Lanolate
	PEG-27, 30 Lanolin
	PEG-5 Octanoate
	PEG-5, 10 Soy Sterol
	PEG-2, 6, 8, 9, 20, 30, 32 Stearate
	Cetearyl Glucoside
	Methyl Glucose Sesquistearate
	Sucrose Distearate
	Sucrose Stearate
	Glyceryl Sorbitan Oleostearate
	Glyceryl Sorbitol/Oleate/Hydroxystearate
	Sorbitan Isostearate
	Sorbitan Oleate
	Sorbitan Sesquioleate
	Sorbitan Stearate
	PEG-1, 3 Glyceryl Sorbitan Isostearate
	PEG-20 Sorbitan Oleate
	PEG-40 Sorbitan Peroleate
	PEG-40 Sorbitol Hexaoleate
	Polysorbat 20, 40, 60, 65, 80, 85
	C20-40 Cholesterol/Lanosterol Esters
	Cholesterol
	Hydrogenated Tallow Glycerides

	Lanolin Lanolin Alcohol Cetyl Dimethicone Copolyol Laurylmethicone Copolyol
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With respect to the solvent or mixture of solvents present in the second compartment(s) (compartment type B) of the inventive microcapsule it is also or alternatively contemplated that the mixing of the one or more sunscreen agent(s) present in the first compartment(s) (compartment type A) with the solvent(s) after exposure to UV radiation such as sun light leads to a further, preferably synergistic, effect on the UV protective properties of the microcapsule: the solvent(s) present in the second compartment(s) are preferably chosen such that these have also an "activating" effect (with respect to UV absorbing/reflecting/scattering of UV radiation) on the sunscreen agent(s) in the first compartment(s). Thus, according to preferred embodiments of the microcapsule of the present invention the sunscreen agent(s) in the first compartment(s) scatter(s), absorb(s) and/or reflect(s) more UV radiation in the solvent or mixture of solvents when the sunscreen(s) mixes/mix with the solvent or mixture of solvents upon exposure of the microcapsule to an effective amount of UV radiation/visible light than said sunscreen agent(s) present in the first compartment would do before being exposed to an effective amount of UV radiation/visible light (i.e. without contact to the solvent(s) present in the second compartment(s)). In other words, before exposure of the microcapsule according to the present invention to UV radiation and/or visible light, the sunscreen agent(s) in the first compartment(s) are present in pure form or dissolved or suspended in a solvent (or mixture thereof) wherein said sunscreen agent(s) has/have at least for a certain wavelength or range of wavelengths belonging to the UV part of the electromagnetic spectrum a lower extinction coefficient (i.e. show a lower UV absorbance for that wavelength or range of wavelengths) and/or less reflecting and/or scattering properties with respect to such wavelength(s) of UV radiation compared to the corresponding properties (absorbance/reflectance/scattering) of the sunscreen agent(s) with respect to that/those UV wavelength(s) when in contact (in particular mixed) with the solvent(s) present in the second compartment(s).

The underlying principle of this preferred "solvent shift" effect embodied in preferred forms of the inventive microcapsule, e.g. when present in a cosmetic formulation, can be summarized as follows:

The efficacy of sunscreens depends on the solvents in which they are dissolved. Changes in both the wavelength of maximum absorbance and molar absorption are typically observed

for many sunscreen-solvent systems studied. Many sunscreens exhibit excellent protection against UVB radiation in one solvent while only moderate or low protection against UVB in a different solvent. Thus, in the context of cosmetic/dermatological sun protection the choice of the solvent for a particular UV filter determines the efficiency of sun protection and consequently the SPF of a sunscreen formulation.

Alternatively, many sunscreens exhibit excellent protection against UVA radiation in one solvent while only moderate or low protection against UVA in a different solvent. Thus, in the context of cosmetic/dermatological sun protection the choice of the solvent for a particular UV filter determines the efficiency of UVA protection and consequently may compensate photodegradation that is typical to many UVA filters used in sunscreen formulations.

For example, Agrapidis et al. (J. Soc. Cosmet. Chem., 38, 209-221, 1987) studied solvatochromic shifts of UV filters in solvents of varying polarity. The authors determined strong solvatochromic shifts for several of UV filters by changing solvent polarity. The authors gave recommendations on which filters perform best in which solvent (in a cosmetic context).

Therefore, the present invention provides photoresponsive microcapsules preferably containing UV filters in compartment A and an activating solvent of "optimal" polarity in compartment B.

Alternatively, the present invention provides photoresponsive microcapsules preferably containing UV filters in compartment A in a deactivating solvent of "non-optimal" solvent polarity and an activating solvent of "optimal" polarity in compartment B.

Other solvatochromic shifts were observed by Castro et al. (Spectrochimica Acta Part A 59: 2685-2696, 2003). The authors studied solvents with varying ion concentrations, in particular the influence of certain metal ions. In this study it was determined that in particular aluminum ions, when present in the solvent, form complexes with UV filters and change the absorbance spectra of UV filters converting a strong UV filter into a weak UV filter.

Thus, according to further preferred embodiments, the present invention provides microcapsules containing UV filters dissolved in a "deactivating" solvent of non-optimal ion composition in compartment A.

In the context of the present invention it is particularly useful to place into compartment A one or more UV filters in a “deactivating” solvent and in compartment B an “activating” solvent (possibly in combination with UV filters other than in compartment A). (UV- and/or visible) Light-induced mixing of both compartments activates or at least partially activates the UV filter(s) (of compartment A).

“Activation” of UV filters means increasing the protection strength at a desired wavelength of UV radiation.

An “activating” solvent is a solvent in which a given UV-filter has more protection in the UVA/UVB range. A “deactivating” solvent is defined as a solvent where a given UV-filter has less protection in the UVA/UVB range.

Since UVB radiation is mostly responsible for sunburn (see Fig. 1), a particularly preferred deactivating solvent is a solvent in which a given UV filter has less protection in the UVB range and a preferred activating solvent is a solvent in which a given UV filter has more protection in the UVB range.

Since UVB radiation of 307 nm is most effective to cause sunburn (Fig. 1), a highly preferred deactivating solvent is a solvent in which a given UV filter has less protection at 307 nm in the UVB range and a highly preferred activating solvent is a solvent in which a given UV filter has more protection at 307 nm.

Since many commercial UVA filters degrade in sunlight, losing their protective strength, a preferred deactivating solvent is a solvent in which a given UV filter has less protection in the UVA range and a preferred activating solvent is a solvent in which a given UV filter has more protection in the UVA range.

The microcapsule of the invention may, as will be apparent to the skilled person, comprise any suitable material and may be prepared from materials and by methods well known in the art, including as generally described in "Functional Coatings" (Ed. Ghosh, 2006, WILEY-VCH Verlag, Weinheim), "Microencapsulation: Methods and Industrial Applications" 2nd Edition (Ed. Benita, 2006, CRC Press) and "Spray drying handbook" 5th Edition (Ed. Masters, 1994, 1994, Longman Group). Preferably, the microcapsule has an outer shell comprising a material selected from the one that belongs to a class of materials selected from the group consisting of: aromatic polymers, diene polymers, epoxy resins, heteroaromatic polymers, heterocyclic polymers, inorganic polymers, phenolic polymers, phenolic resins, poly

heterocyclic polymers, poly(α -olefins), polyacetals, polyacrylates, polyalkynes, polyamides, polyaramides, polyesters, polyethers, polyimides, polyisocyanides, polymethacrylates, polyolefines, polysiloxanes, polysulfides, polyureas, polyurethanes, vinyl polymers, vinylidene polymers and perfluoralkoxy polymers.

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More preferably, the microcapsule has an outer shell comprising a material selected from the group consisting of: alkyd resins, bisphenol-A polysulfone, carboxylated ethylene copolymers, Nylon 11, Nylon 12, Nylon 3, Nylon 4,6, Nylon 6, Nylon 6 copolymer, Nylon 6,10, Nylon 6,12, Nylon 6,6, Nylon 6,6 copolymer, Nylon MXD6, silicium dioxide (glass) by
 10 sol gel encapsulation, poly(1,3-dioxepane), poly(1,3-dioxolane), poly(1,4-phenylene vinylene), poly(2,6-dimethyl-1A-phenylene oxide), poly(4-hydroxy benzoic acid), poly(4-methyl pentene-1), poly(4-vinyl pyridine), poly(acetylene), poly(acrylamide), poly(acrylic acid), poly(benzimidazol) (PBI), poly(benzobisoxazol) (PBO), poly(benzobisthiazol) (PBT), poly(butadiene) (PBD), poly(butene-1), poly(butyl methacrylate), poly(butylene terephthalate)
 15 (PBT), poly(chloral), poly(chloro trifluoro ethylene), poly(chloroprene), poly(cyclohexyl methacrylate), poly(di-n-butyl siloxane), poly(di-n-hexyl siloxane), poly(di-n-hexyl silylene), poly(di-n-pentyl siloxane), poly(di-n-propyl siloxane), poly(diethyl siloxane), poly(dimethyl siloxane), poly(dimethyl silylene), poly(diphenyl siloxane), poly(ether ether ketone), poly(ether imide), poly(ether ketone), poly(ether sulfone), poly(ethyl acrylate), poly(ethyl
 20 methacrylate), poly(ethylene-2,6-naphthalate), poly(ethylene), poly(hydridosilsesquioxane), poly(m-phenylene isophthalamide), poly(methacrylic acid), poly(methyl acrylonitrile), poly(methylene oxide), poly(methylphenyl siloxane), poly(methylsilimethylene), poly(methylsilsesquioxane), poly(n-butyl isocyanate), poly(N-methylcyclodisilazane), poly(N-vinyl carbazole), poly(N-vinyl pyrrolidone), poly(p-benzamide), poly(p-chlorostyrene), poly(p-methyl styrene), poly(p-phenylene oxide), poly(p-phenylene sulfide), poly(p-xylylene),
 25 poly(phenyl/tolylsiloxane), poly(phenylsilsesquioxane), poly(propyl methacrylate), poly(propylene), poly(pyromellitimide-1.4-diphenyl ether), poly(sulfur nitride), poly(tetrahydrofuran), poly(thiophene), poly(trimethylene oxide), poly(urea), poly(urethane), poly(vinyl acetate), poly(vinyl alcohol), poly(vinyl butyral), poly(α -methylstyrene), poly(-
 30 caprolactone) and any other material disclosed herein.

Most preferably the microcapsule has an outer shell comprising a polymer or co-polymer selected from the group consisting of: poly(acrylonitrile (PAN), poly(carbonate) (PC), poly(chlorotrifluor ethylene) (PCTFE), poly(ether sulphone) (PES), poly(ethylene oxide) (PEO),
 35 poly(ethylene terephthalate) (PET), poly(ethylene-co-vinyl acetate), poly(ethylene-co-vinyl alcohol), poly(ethylene) high density (HDPE), poly(ethylene) low density (LDPE), poly(methyl methacrylate) (PMMA), poly(methyl trifluoro propyl siloxane), poly(p-phenylene

terephthalamide) (Aramid), poly(perfluor ethylen propylen (FEP), poly(perfluoralkoxyl alkan) (PFA), poly(propylene) (PP), poly(styrene-acrylonitrile) (SAN), poly(styrene-co-methyl methacrylate) (SMMA), poly(styrene) (PS), poly(tetrafluor ethylen) (Teflon), poly(vinyl chloride) (PVC), poly(vinyl fluoride) (PVF), poly(vinylidene chloride) (PVDC) and
5 poly(vinylidene fluorid) (PVDF).

The separation (border) between the UV filter(s) in the first compartment and the contents (in particular solvent or mixture of solvents) present in the second compartment is at least partially removed by a radiation containing a UV and/or visible part, preferably sunlight or
10 simulated sunlight, such that UV filter(s) and solvent(s) that were previously separated mix. Preferably, UV/VIS light directly or indirectly ruptures the separation, for example a polymer membrane, between first compartment (UV filter(s)) and second compartment (solvent(s)).

Photoresponsive materials forming the border between the compartments in the inventive
15 microcapsule may become at least partially permeable by a number of mechanisms. For example, the border material may become completely and non-selectively permeable by the (at least partial) removal of the separation formed by the material. Such removal can be brought about by photochemical rupture of the separation such that the physical separation is no longer operative.

20 Photochemical rupture of separating materials in the context of the invention can be achieved by including within the first compartment(s) a photolabile compound that generates a gas (e.g. nitrogen or carbonoxides) which increases internal pressure that finally ruptures the compartment. Corresponding techniques are known in the art, see. US Patent No.
25 3,301,439, US 4,898,734 and Mathiowitz et al. (1981) J. Appl. Polymer Sci. 26, 809-822. Further methods to produce gases by UV radiation include, but are not limited to:

- photodecomposition of ammonium oxalate (forming gaseous ammonia and gaseous carbon dioxide; non-toxic example); see Nair et al. (1976) J. Phys. Chem. Vol. 80 No. 23, 2552-2555;
- 30 - UV radiation-induced decomposition of dibenzoyl peroxide (DBP) resulting in the formation of gaseous carbon dioxide, a mechanism known since the 1950s;
- UV radiation-induced decomposition of azo-bis-(isobutyronitrile) (AIBN) resulting in the formation of gaseous nitrogen (see US 3,301,439, US 4,898,734 and Mathiowitz et al., *supra*);
- 35 - UV radiation-induced decomposition of *ortho*-nitrodimethoxyphenylglycine (see Woodrell et al. (1999) Org. Lett. Vol. 1, No. 4, 183-185.

- photodecomposition of azodicarbonamide (see Mathiowitz, et al., Journal of Membrane Science, 40 (1989) 67-86)

Similar to photochemical rupture of the border between first and second compartment(s), the (at least partial) removal of the separation can be further achieved by using photolabile materials (e.g. photolabile polymers, photolabile polymer-nanocomposites) that degrade, for example that depolymerize or decompose, under UV radiation, e.g. by photodecrosslinking of o-nitrobenzyl alcohol containing polymers or by photodecrosslinking of polymers containing cinnamate dimers, or by photodecrosslinking of polymers containing coumarin dimers. Such photochemical degradation can completely remove the separation feature, or only remove or degrade portions or parts of the material and hence render the separation component permeable or partially permeable to the sunscreen agent(s) and/or solvent(s).

Correspondingly, photocatalytic degradation, such as decomposition, techniques of encapsulating materials based on a radical mechanism have been recently described by Katagiri et al. (2009) Chem. Mater. Vol. 21, No. 2, 195-197. Sensitized photodecomposition of polymers by UV (UVA/UVB) radiation is known in the art as well (see Torikai et al. (1998) Polymer Degradation and Stability 61, 361-364 (using beta-carotene as photosensitizer) and Torikai et al. (1995) J. Polymer Sci: Part A Polymer Chem. 33, 1867-1871 (using benzophenone as photosensitizer)). Thus, typical photosensitizers of use in this embodiment include carotenes, benzophenones, dibenzoylmethanes, coumarin derivatives, quinines, such as p-benzoquinone, hydroquinone, xanthene dyes, benzoflavine, or setoflavin, 9,10-anthraquinone, benzophenone, 2-chlorothioxanthone, 9-fluorenone and thioxanthone. Other sensitizers include 2-acetonaphthone, ketobiscoumarins and 2-acetonaphthone. The person skilled in the art understands that such photosensitizers could be incorporated in the polymer membrane, the first compartment(s) and/or the second compartment(s).

Further possible mechanisms of degradation employ: (i) the photocleavage of co-polymers containing photolabile monomers within the polymer backbone as break points (see Subramanian (2002) European Polymer Journal 38, 1167-1173); and/or (ii) photodecrosslinking of a crosslinked material such as a polymer or particles (see Yuan, (2005), Langmuir 21, 9374-9380).

Photochemical rupture of the separation between first and second compartment(s) can be further achieved by including organic polymer-TiO₂ nanocomposites. TiO₂ acts as photocatalyst to decompose the capsule structure. Photoactive TiO₂ nanoparticles can also be incorporated in an inner polyelectrolyte shell. TiO₂ nanoparticles adsorbed in an inner

polymer shell act as microheterogeneous photocatalysts performing redox reactions (electron donor/acceptor reactions) with the polymer leading to the photodecomposition of the polymer.

- 5 The UV radiation-induced (at least partial) removal of the separation (border) between first and second compartment(s) in the inventive microcapsule may also be achieved by including in one of the compartments, preferably the second compartment(s), a photoacid or photobase progenitor compound and to use an acid or base, respectively, sensitive material such as an acid or base sensitive polymer for forming the border between the first and
- 10 second compartment(s) which at least partially degrades under acidic or basic, respectively, conditions. Preferred polymers for this aspect of the present invention are polyamides, polyesters and polycarbonates. Specific examples of this type of polymers may be found in the capsule (outer shell) materials listed above.
- 15 Photoacid progenitor compounds useful in this context of the present invention include onium salts, 2-nitrobenzyl esters of sulfonic acids, 2 nitrobenzyl esters of carboxylic acids, imino sulfonate, 1-oxo-2-diazonaphthoquinone-4-sulfonate derivatives, 1-oxo-2-diazonaphthoquinone-5-arylsulfonate derivatives, N-hydroxyimide sulfonate, tri(methanesulfonyloxy)-benzene, triarylphosphate derivatives, azophenol derivatives,
- 20 naphthol derivatives, 4-phenoxyphenyl)diphenylsulfonium triflate, nitro-substituted aromatic aldehydes, 2-hydroxyphenyl-1-(2-nitrophenyl)ethyl phosphate, 1-(2-nitrophenyl)ethyl sulfate and spirooxazine photochromes.

- Photobase progenitor compounds useful in this context of the present invention include
- 25 carbamates, O-acyloximes, ammonium salts, sulfonamides, formamides, nifedipines, α -aminoketones, acridine, 6-methoxyquinoline, styrene, 2-vinylnaphthalene, 2-naphthylacetylene, nitro-substituted phenylacetylenes, nitro-substituted phenylalkenes, p-nitrophenylacetylene, hydroxyl-substituted vinylnaphthalenes, hydroxyl-substituted naphthylacetylenes, o-hydroxystyrene, methoxy-substituted benzyl alcohols, dimethoxy-
 - 30 substituted benzylalcohols, triphenylmethane leucohydroxide derivatives, 9-phenylxanthen-9-ol, trans-retinol, dibenzosuberol, 5-suberol, diarylmethanol, triarylmethanol, pyridoxine and 9-hydroxy fluorine.

- According to the present invention it is also contemplated that not only the separation
- 35 between the first and second compartment may partially be removed, as disclosed herein, upon exposure to UV radiation, but also the outer microcapsule shell may rupture, degrade

or decompose using the materials and compounds as described for the separation between the first and second compartment(s).

According to certain embodiments of the invention, the term "microcapsules" relates to structures having an average diameter ranging from 5 nm to 200 μm , preferably from 10 nm to 10 μm . However, in other embodiments of the invention, "microcapsules" relate to a structure that has an average largest dimension, preferably a diameter, of between about 10 nm and 1 mm, preferably between about 50 nm and 500 μm , such as about 100, 150, 200, 500, 750 nm, or about 1, 2, 10, 20, 50, 75, 100 or 250 μm .

In microcapsules according to the invention having a single core structure (Fig. 3), the core compartment (first compartment or compartment A) typically has an average diameter of from 0.1 μm to 75 μm . Multi core structures may be made of solid sunscreen agents (for example a crystalline sunscreen agent such as crystalline sulisobenzone, or PABA) coated or grafted with a preferably UV-sensitive polymer coating and such cores (first compartments) can have very small diameters down to 10 nm.

The first compartment(s) in the inventive microcapsule generally make up 1 to 75 %, preferably 5 to 50 %, more preferably 10 to 30 %, by volume of the microcapsule.

The microcapsules according to the invention may be derived from different microencapsulation processes including extrusion techniques, spray-drying, fluid bed coating, rotating disk, coacervation, solvent evaporation, phase separation, *in situ* polymerization, interfacial polymerization, miniemulsion, sol gel encapsulation, layer by layer assembly, or can be derived from colloidosomes (see: Hsu, et al., Langmuir 2005, 21, 2963-2970).

A preferred embodiment of a method for the preparation of microcapsules according to the invention having single core, multiple core or multiple shell structures comprises the steps of:

- (a) preparing a first compartment by forming a polymer shell around a droplet or particle of at least one sunscreen agent as defined herein or around a droplet of a solution or suspension of at least one sunscreen agent as defined herein;
- (b) combining the first compartment with a solvent or mixture of solvents as disclosed herein for said at least one sunscreen agent; and
- (c) forming a polymer shell around the combination of (b);

wherein the polymer shell formed in step (a) becomes at least partially permeable for said at least one sunscreen agent and/or for said solvent or mixture of solvents upon exposure to an effective amount of UV radiation and/or radiation in the visible spectrum.

5 Polymers useful for this method have been described in detail above.

As will be readily appreciated by the skilled person upon the disclosure of the present invention, the particular constituents of microcapsules or formulations of the invention may vary depending on its desired application or properties. For example, by varying the
10 amounts, identity and concentrations of the compounds such as the sunscreen agent(s), solvent(s) etc., the characteristics or properties of the microcapsule or formulation may be varied as desired. In particular, the material used or dimension/thickness of microcapsules of the invention may vary as required in order to achieve a particular property, such as the sensitivity of the photoresponsive system to UV and/or VIS radiation.

15 The present invention is therefore further directed to a cosmetic composition containing the inventive microcapsules as defined above together with a cosmetically acceptable carrier. Also, the present invention is directed to a medical (in particular, dermatological) composition containing the microcapsules as defined above together with a dermatologically acceptable
20 carrier. Such formulations may be described as "photoresponsive".

The adaptable sun protecting properties of a composition according to the invention can be expressed or otherwise characterised by the change of Sun Protection Factor (SPF; see above for definition) upon exposure of the composition to UV and/or VIS radiation. Preferred
25 compositions of the present invention show, upon exposure to UV and/or VIS radiation, an increase of at least 1, more preferably about 2, about 3, about 4 or about 5 to about 50, preferably about 10, 15, 20, 25, 30, 35 or 40 or more SPF units compared to the composition before exposure to UV and/or VIS radiation. As well as characterising this change in SPF by an absolute amount, the change may also be expressed as a relative change in SPF of the
30 composition according to the invention. In certain embodiments, the SPF of such a composition upon exposure to UV and/or VIS radiation may be at least about 2 times (or fold) to about 25 times, greater than said composition shows before exposure to UV and/or VIS radiation, preferably about 5, 10, 15 or 20 times (or fold) greater. For example, an initial SPF of 2 may increase by 20-fold to show an SPF of about 40. It will be understood however, that
35 such a relative change in SPF cannot exceed the maximum SPF protection currently measureable, i.e. cannot exceed an absolute SPF value of about 45 or 50.

The adaptive sun protection properties of compositions according to the present invention as outlined before may further be controlled with respect to the rate of change of the SPF over time. It is apparent for the skilled person that the above term "change of SPF upon exposure to UV and/or VIS radiation" can either mean a relative change from the starting situation (i.e. before exposure to UV/VIS radiation) to an intermediate status after UV/VIS exposure or an absolute change of the SPF starting before UV/VIS exposure to a maximum SPF. It is clear for the skilled person that the SPF change develops over time. Thus, by adjustment of multiple factors known to the skilled person such as, in particular, thickness of the (inner) polymer membrane(s), size or size distribution of first compartment(s) (e.g. inner core(s) of a microcapsule having single or multiple core structure), use of microcapsules having different characteristics ("fast" responding capsules, "slow" responding capsules, as outlined above), solvent selection (e.g. creating "slow" responding capsules by using high viscosity components like emollients) and so on (and disclosed in more detail elsewhere herein), the rate of SPF change of a composition according to the invention can be adapted to the particular needs. For typical compositions according to the invention the change from their starting SPF to the maximum SPF takes around 0.5 to 6 hours, more preferably, 2 to 4 hours such as 2, 2.5, 3, 3.5 or 4 hours.

According to the present invention the terms "cosmetically acceptable carrier" and "dermatologically acceptable carrier" are used interchangeably and relate to a corresponding base composition comprising conventional cosmetic and/or pharmaceutical vehicles and/or diluents and/or adjuvants and/or additives and/or additional active ingredients.

The microcapsule of the invention for use in medicine, or the dermatological formulation comprising the same, may not differ in physical composition from the microcapsule of the invention when used for non-medical purposes or from the cosmetic sunscreen formulation. However, in certain embodiments the microcapsule of the invention for use in medicine, or the dermatological formulation, may include additional active ingredients. For example, such microcapsules or formulations may include pharmaceutically active ingredients such as soothing agents, analgesics, moisturisers, anti-inflammatory agents, anti-infective agents, wound-healing agents and/or anti-cancer agents such as anti-melanoma agents.

The sunscreen formulations (such as the cosmetic and/or the dermatological formulation) according to the invention may comprise (in addition to the sunscreen agent(s) present in the microcapsule as defined above) one or more further sunscreen agent(s) which may be selected from any known organic or inorganic sunscreen agents, for example those as defined above.

In certain embodiments the at least one further organic sunscreen agent is a combination of at least two sunscreen agents: a UVA sunscreen agent and a UVB sunscreen agent. The skilled person will readily appreciate whether an organic sunscreen agent is a "UVA" or a "UVB" sunscreen agent. In other certain embodiments, the at least one further organic sunscreen agent is one that shows limited sensitivity to changes in pH in regards to UV absorption, including the sunscreen agents butyl methoxydibenzoylmethane, ethylhexyl methoxycinnamate or cinoxate.

In certain embodiments, the microcapsule or (cosmetic or dermatological) formulation of the invention includes both an inorganic sunscreen agent and at least one further organic sunscreen agent (in each case as specified or defined above), preferably a combination of at least two sunscreen agents: a UVA sunscreen agent and a UVB sunscreen agent.

In certain preferred embodiments, the inorganic sunscreen agent and/or the at least one further organic sunscreen agent is present in the microcapsule or formulation in an amount to provide a composition or formulation that before exposure to UV radiation shows an SPF of between 1 and 45, preferably an SPF of about 2, 5, 10, 15, 20, 25, 30, 35 or 40.

The cosmetic sunscreen formulation of the present invention, or the dermatological formulation of the invention, may be in the form of a suspension or dispersion in solvents or fatty substances, or alternatively in the form of an emulsion or micro emulsion (in particular, of O/W or W/O type, O/W/O or W/O/W-type, wherein O stands for oil phase and W stands for water phase), such as a cream, a paste, a lotion, a thickened oil or a milk, a vesicular dispersion in the form of an ointment, a gel, a solid tube stick or an aerosol mousse, may be provided in the form of a mousse, for a foam or spray foams, sprays, sticks or aerosols or vibes. Examples of cosmetic or dermatological preparations are skin care preparations, in particular, body oils, body lotions, body gels, treatment creams, skin protection ointments, moisturizing gels, moisturizing sprays, revitalizing body sprays or lip stick formulations.

The microcapsules, cosmetic compositions such as a cosmetic sunscreen formulation, or dermatological formulations for use in the present invention may further comprise usual cosmetic or dermatological adjuvants and/or additives such as preservatives/antioxidants, fatty substances/oils, water, organic solvents, silicones, thickeners, softeners, emulsifiers, additional light screening agents, antifoaming agents, moisturizers, frequenters, surfactants, fillers, sequestering agents, anionic, cationic, non-ionic or amphoteric polymers or mixtures thereof, propellants, acidifying or basifying agents, dyes, colorants, pigments or

nanopigments, light stabilizers, insect propellants, skin tanning agents, skin whitening agents, antibacterial agents, preservative active ingredients or any other ingredients usually formulated into cosmetic or dermatological preparations.

- 5 The necessary amount of the cosmetic/dermatological adjuvants, additives and/or additional active ingredients can, based on the desired end product, easily be chosen by a person skilled in the art.

10 In preferred modes of practicing the invention, the cosmetic or dermatologic adjuvants, additives and/or additional active ingredients comprise a buffered environment, preferably an environment buffered to a pH of between about 4.0 to about 9.0, such as a pH of about 4.5, 5.0, 5.5, 6.0, 6.5, 7.0, 7.5, 8.0 or 8.5.

15 The present invention further relates to a cosmetic method for protecting human skin and/or hair against UV radiation comprising the step of applying an effective amount of the cosmetic sunscreen formulation onto (usually human or animal) skin and/or hair.

20 The photoresponsive microcapsules as defined above are for use in medicine (for example for the manufacture of pharmaceutical, in particular dermatological preparations), especially for the prevention of skin cancer or sunburn. The invention is therefore also directed to a medical method comprising the application of an effective amount of the dermatological formulation onto (preferably human or animal such as pig) skin and/or hair.

25 From the foregoing description it is also evident that the present invention provides a method for modifying the SPF or the Boots star rating of a cosmetic or dermatological formulation as defined above comprising the step of exposing said formulation to an effective amount of UV radiation and/or radiation in the visible spectrum.

30 The figures show:

Fig. 1 shows a graphical representation of irradiance ($\text{W/m}^2/\text{mm}$) versus wavelength of radiation.

35 Fig. 2 shows a table and corresponding graphical representation of the relation between Sun Protection Factor and % of total absorbed UV radiation.

Fig. 3 shows an embodiment of a microcapsule of the invention having a single core structure.

Fig. 4 shows an embodiment of a microcapsule of the invention having a multi (i.e. multiple) core structure.

Fig. 5 shows an embodiment of a microcapsule of the invention having a multiple layer (i.e. multiple shell) structure.

The following non-limiting examples further illustrate the present invention:

EXAMPLES

Preparation of photoresponsive sunscreen composition

Preparation of inner core from colloidosomes:

The method was adapted as described previously (see Hsu, et al, Langmuir 2005, 21, 2963-2970). Briefly, the protocol is as follows: use polystyrene particles crosslinked with divinylbenzene having carboxyl surface charge groups (DVB carboxyl particles) with an average diameter of 0.5 μm (Interfacial Dynamics Corporation, IDC). Suspend 3 g of polystyrene particles in 97 g water/glycerol (15% w/w). To create shells that encapsulate UV filter droplets, add 10 g of the UV filter Parsol SLX (Polysilicone-15; DSM) to 100 g of the aqueous polystyrene particle suspension and additionally add 0.2 g of micronized photoactive TiO_2 particles. Homogenize with an IKA Ultra Turrax for 5 min at 5000 rpm to form an oil-in-water (o/w) emulsion. Polystyrene particles and TiO_2 particles self-assemble at the interface of the UV filter oil droplets to minimize total interfacial energy, thus forming UV filter droplets with an average diameter of 10 μm coated with polystyrene particles. The suspension is subsequently subjected to heating in order to sinter the polymer particles. Sintering of polystyrene particles entails heating in an oven to 105 $^{\circ}\text{C}$, slightly above the glass transition temperature of polystyrene particles. Individual PS particles sinter (=melt and fuse) forming an impermeable polymer shell with photoactive TiO_2 microparticles integrated into the polymer shell, enclosing in its interior the UV filter. The prepared photoresponsive inner cores of the microcapsules have an average diameter of 10 μm .

Preparation of outer shell:

The outer shell of the particles is prepared as follows: Suspend 2.5 g of encapsulated UV filters (prepared as described above) in 10 g of a solution containing paraffin oil (95% w/w,

SigmaAldrich), terephthaloyl chloride (5% w/w, SigmaAldrich). Add 50 ml of a solution containing deionized water (98% w/w) and polyvinylalcohol, PVA (2%, w/w, SigmaAldrich). Gently emulsify using a rotor-stator homogenizer (Ultraturrax, T25, IKA-Labortechnik) at 500 rpm for 20 min at 15°C. During emulsification the paraffin oil suspension forms small droplets in the water phase. Add this emulsion to 50 ml of a solution containing deionized water (68%, w/w), polyvinylalcohol, PVA (2%, w/w, SigmaAldrich) and diethylenetriamine (30% w/w, SigmaAldrich). Now the interfacial polymerization starts. Terephthaloyl chloride, (present in the oil phase) and diethylenetriamine (present in the aqueous phase) polymerize at the oil-water interface forming a polymer shell around the cores containing the UV filter. The reaction is continued for 2 hours with gentle stirring at 20°C. Single core photoresponsive microcapsules are isolated by filtration and repeatedly washed with hexane and finally dried.

Preparation of cosmetic carrier:

Preparation of a photoresponsive cosmetic sunscreen composition: gently mix jojoba oil (2% w/w), cocoa butter solid (2% w/w), isocetyl alcohol (15% w/w), fragrance (1% w/w), vitamin E acetate (0.1% w/w), mineral oil (29% w/w), octyl palmitate (25,9 w/w), and finally add photoresponsive microcapsules (25% w/w) prepared as described above.

SPF Assay

In vitro SPF assay: sample is evenly spread over the surface of a roughened PMMA plate (Helioplates from Helioscience, Marseille, France, 16 cm², specific roughness: Ra = 6–7 lm) at 1.2 mg/cm² and is allowed to settle for 20 min. After irradiation with a Phillips Sun Simulator (Type HB 175/A) for various periods of time the in vitro SPF is measured using an Optronic OL 754 Spectroradiometer containing an integrating sphere behind the sample and using a double monochromator/photo multiplier tube (PMT) detection system.

Results:

Time points (in min)	In vitro SPF
0	7
20	11
60	15
180	20

Claims

1. A photoresponsive microcapsule comprising one or more first compartment(s) containing at least one sunscreen agent and one or more second compartment(s) containing a solvent or mixture of solvents for said sunscreen agent(s) but containing substantially no sunscreen agent(s) present in the first compartment(s) wherein the border between the first and second compartments becomes at least partially permeable for the sunscreen and/or the solvent or mixture of solvents upon exposure to an effective amount of UV radiation and/or radiation in the visible spectrum.
2. The microcapsule of claim 1 wherein the first compartment(s) constitute(s) from 1 to 75 % by volume of the microcapsule.
3. The microcapsule of claim 1 or 2 wherein, upon exposure of the microcapsule to an effective amount of UV radiation and/or radiation in the visible spectrum, the distribution of the sunscreen agent(s) in the microcapsule becomes substantially homogenous within the microcapsule.
4. The microcapsule of claim 3 wherein, upon exposure of the microcapsule to an effective amount of UV radiation and/or radiation in the visible spectrum, the concentration of the sunscreen agent(s) is of from 1 to 75% by weight, preferably 5 to 50 % by weight, more preferably 10 to 40 % by weight, particularly preferred 15 to 30 % by weight of the microcapsule.
5. The microcapsule according to any one of the preceding claims wherein the border between the first and second compartment(s) comprises a polymer which, upon exposure to an effective amount of UV radiation and/or radiation in the visible spectrum, directly or indirectly becomes at least partially permeable for the sunscreen(s) and/or solvent or mixture of solvents, respectively, or ruptures.
6. The microcapsule of claim 5 comprising an outer polymer shell and having one or more first compartment(s) having an inner polymer shell within the microcapsule.

7. The microcapsule of claim 6 wherein the first compartment(s) has/have an average diameter of 0.01 μm to 75 μm and the microcapsule has an average diameter of from 10 to 200 μm .
- 5 8. The microcapsule of claim 5 or 6 wherein the microcapsule comprises multiple first compartments.
9. The microcapsule according to any one of the preceding claims wherein the first compartment(s) and/or the polymer forming the border between the first and second compartment(s) contain(s) at least one photolabile compound that generates a gas upon exposure to UV radiation and/or radiation in the visible spectrum.
- 10 10. The microcapsule of claim 9 wherein the photolabile compound is selected from the group consisting of ammonium oxalate, iron oxalate, dibenzoyl peroxide, azo-bis-(isobutyronitrile), azodicarbonamide and ortho-nitrodimethoxyphenylglycine.
- 15 11. The microcapsule according to any one of claims 5 to 10 wherein the polymer forming the border between the first and second compartment(s) is a photolabile polymer or photolabile polymer-nanocomposite that at least partially degrades upon exposure to UV radiation and/or radiation in the visible spectrum.
- 20 12. The microcapsule of claim 11 wherein the photolabile polymer is selected from the group consisting of polymers containing o-nitrobenzyl alcohol groups and polymers containing cinnamate dimers.
- 25 13. The microcapsule of claim 11 wherein the photolabile polymer-nanocomposite is an organic polymer-TiO₂ nanocomposite.
14. The microcapsule according to any one of claims 5 to 10 wherein the second compartment contains a photoacid or photobase progenitor compound and the polymer forming the border between the first and second compartment(s) is an acid or base, respectively, sensitive polymer that at least partially degrades under acidic or basic, respectively, conditions.
- 30 15. The microcapsule of claim 14 wherein the photoacid progenitor compound is selected from the group consisting of onium salts, 2-nitrobenzyl esters of sulfonic acids, 2-nitrobenzyl esters of carboxylic acids, imino sulfonate, 1-oxo-2-diazonaphthoquinone-
- 35

4-sulfonate derivatives, 1-oxo-2-diazonaphthoquinone-5-arylsulfonate derivatives, N-hydroxyimide sulfonate, tri(methanesulfonyloxy)-benzene, triarylphosphate derivatives, azophenol derivatives, naphthol derivatives, 4-phenoxyphenyl)diphenylsulfonium triflate, nitro-substituted aromatic aldehydes, 2-hydroxyphenyl-1-(2-nitrophenyl)ethyl phosphate, 1-(2-nitrophenyl)ethyl sulfate and spirooxazine photochromes.

16. The microcapsule of claim 14 wherein the photobase progenitor compound is selected from the group consisting of carbamates, O-acyloximes, ammonium salts, sulfonamides, formamides, nifedipines, α -aminoketones, acridine, 6-methoxyquinoline, styrene, 2-vinylnaphthalene, 2-naphthylacetylene, nitro-substituted phenylacetylenes, nitro-substituted phenylalkenes, p-nitrophenylacetylene, hydroxyl-substituted vinylnaphthalenes, hydroxyl-substituted naphthylacetylenes, o-hydroxystyrene, methoxy-substituted benzyl alcohols, dimethoxy-substituted benzylalcohols, triphenylmethane leucohydroxide derivatives, 9-phenylxanthen-9-ol, trans-retinol, dibenzosuberol, 5-suberol, diarylmethanol, triarylmethanol, pyridoxine and 9-hydroxy fluorine.

17. The microcapsule according to any one of claims 14 to 16 wherein the acid or base sensitive polymer is selected from the group consisting of polyamides, polyesters and polycarbonates.

18. The microcapsule according to any one of the preceding claims wherein the sunscreen agent(s) scatter(s), absorb(s) and/or reflect(s) more UV radiation in the solvent or mixture of solvents when the sunscreen(s) mixes/mix with the solvent or mixture of solvents upon exposure of the microcapsule to an effective amount of UV radiation and/or radiation in the visible spectrum than said sunscreen agent(s) present in the first compartment would do before being exposed to an effective amount of UV radiation and/or radiation in the visible spectrum.

19. The microcapsule according to any one of the preceding claims wherein the first compartment(s) contain(s) one or more liquid sunscreen agent(s) in pure or solubilised form.

20. The microcapsule according to any one of the preceding claims wherein the first compartment(s) contain(s) one or more solid sunscreen agent(s) in crystalline or amorphous form or in suspension.

21. The microcapsule according to any one of the preceding claims wherein the first compartment(s) contain(s) at least one UVA sunscreen agent and at least one UVB sunscreen agent.

5

22. The microcapsule according to any one of claims 1 to 20 wherein the first compartment(s) contain(s) at least one UVB sunscreen agent and the second compartment(s) contain(s) at least one UVA sunscreen agent.

10

23. The microcapsule according to any one of claims 1 to 20 wherein the first compartment(s) contain(s) at least one UVA sunscreen agent and the second compartment(s) contain(s) at least one UVB sunscreen agent.

15

24. The microcapsule according to any one of claims 1 to 20 wherein the first compartment(s) contain(s) at least one organic sunscreen agent and the second compartment(s) contain(s) at least one inorganic sunscreen agent.

20

25. The microcapsule according to any one of the preceding claims wherein the sunscreen agent(s) is/are selected from the group consisting of organic and inorganic sunscreen agents.

25

26. The microcapsule of claim 25 wherein the organic sunscreen agent(s) is/are selected from the group consisting of anthranilates, benzophenones, benzotriazoles, camphors, cinnamates, dibenzoyl methanes, imidazoles, malonates, para-aminobenzoic acids, phenols, salicylates, phenyl triazines and triazones.

30

27. The microcapsule of claim 25 wherein the inorganic sunscreen agent is a metal oxide having an atomic number ranging from 10 to 40.

28. The microcapsule of claim 27 wherein the metal oxide is selected from the group consisting of TiO_2 and ZnO .

35

29. A cosmetic composition comprising microcapsules according to any one of the preceding claims and a cosmetically acceptable carrier.

30. The composition of claim 29 wherein the SPF of the composition increases by at least 1 SPF unit, preferably at least 5 SPF units upon exposure of the composition to UV radiation and/or radiation in the visible spectrum.

31. A cosmetic method for protecting skin and/or hair against UV radiation comprising the step of applying an effective amount of the composition of claim 29 or 30 to skin and/or hair.

32. A method for preparing the microcapsule according to any one of claims 6 to 28 comprising the steps of:

(a) preparing a first compartment by forming a polymer shell around a droplet of at least one sunscreen agent or of a solution or suspension of at least one sunscreen agent;

(b) combining the first compartment with a solvent or mixture of solvents for said at least one sunscreen agent; and

(c) forming a polymer shell around the combination of (b);

wherein the polymer shell formed in step (a) becomes at least partially permeable for said at least one sunscreen agent and/or for said solvent or mixture of solvents upon exposure to an effective amount of UV radiation and/or radiation in the visible spectrum.

33. Use of the microcapsule according to any one of claims 1 to 28 for the cosmetic protection of skin and/or hair against UV radiation.

34. A method of increasing the SPF of the composition of claim 29 or 30 comprising the step of exposing said composition to an effective amount of UV radiation and/or radiation in the visible spectrum.

35. The method of claim 34 wherein the SPF of the composition increases by at least 1 SPF unit, preferably at least 5 SPF units upon exposure of the composition to UV radiation and/or radiation in the visible spectrum.

36. A method for the preparation of the composition of claim 29 or 30 comprising the step of combining microcapsules according to any one of claims 1 to 28 with a cosmetically acceptable carrier.

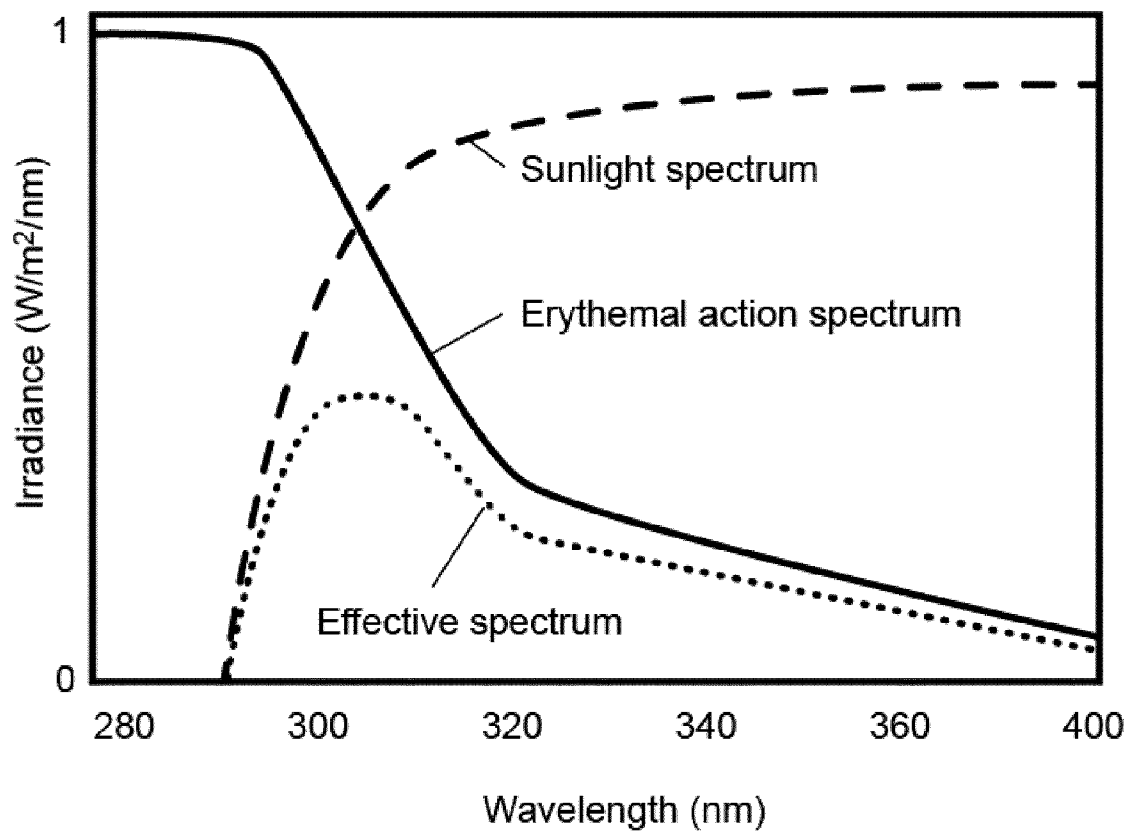


Fig. 1

SPF	Absorbance
2	50.00%
10	90.00%
15	93.33%
20	95.00%
30	96.66%
40	97.50%
50	98.00%

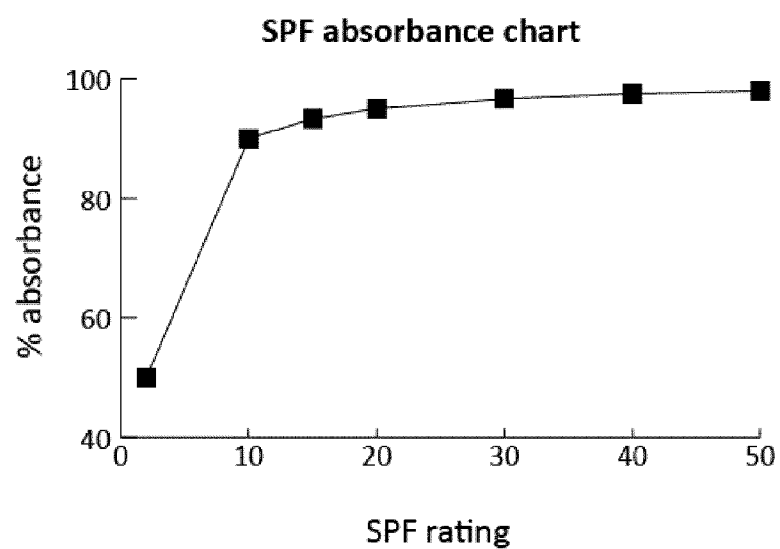


Fig. 2

Single core microcapsules

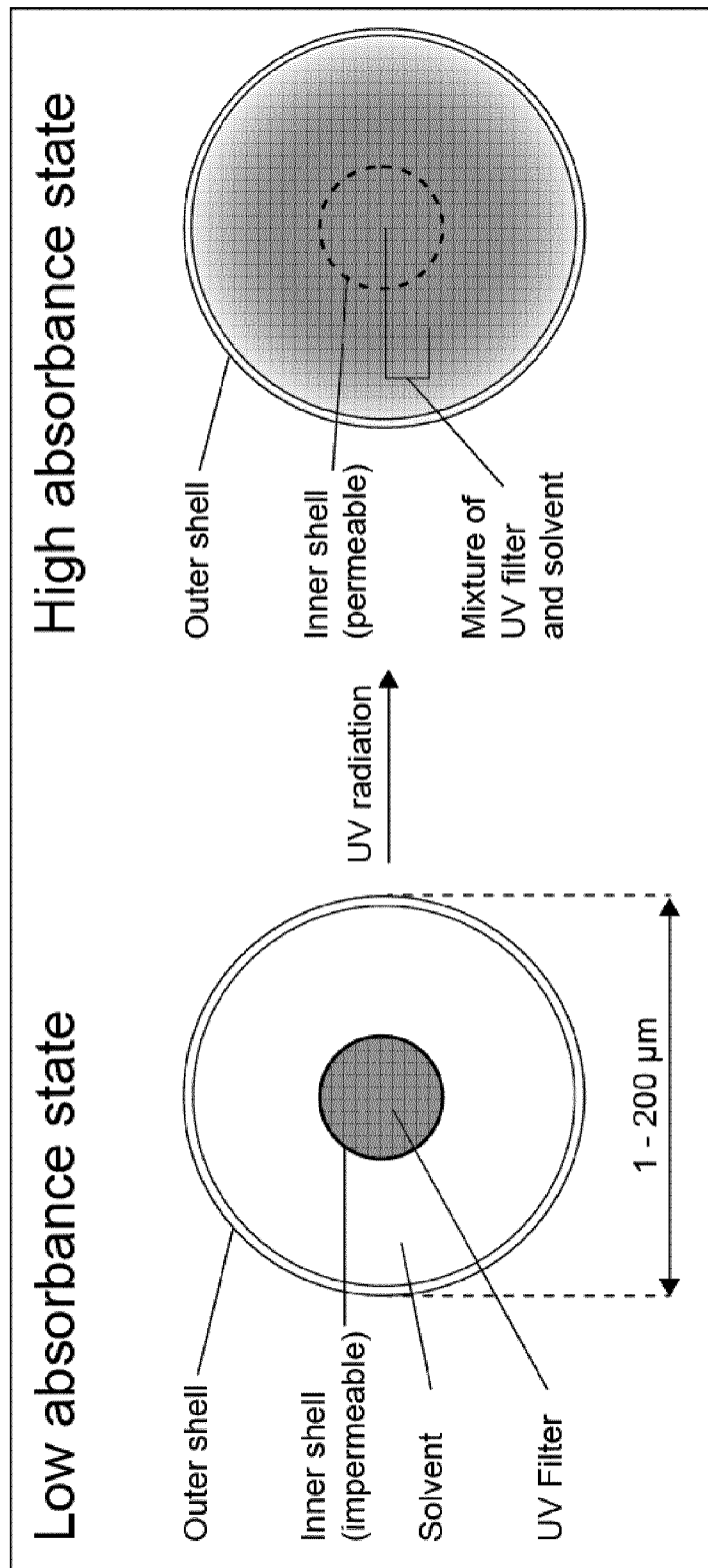


Fig. 3

Multi core microcapsules

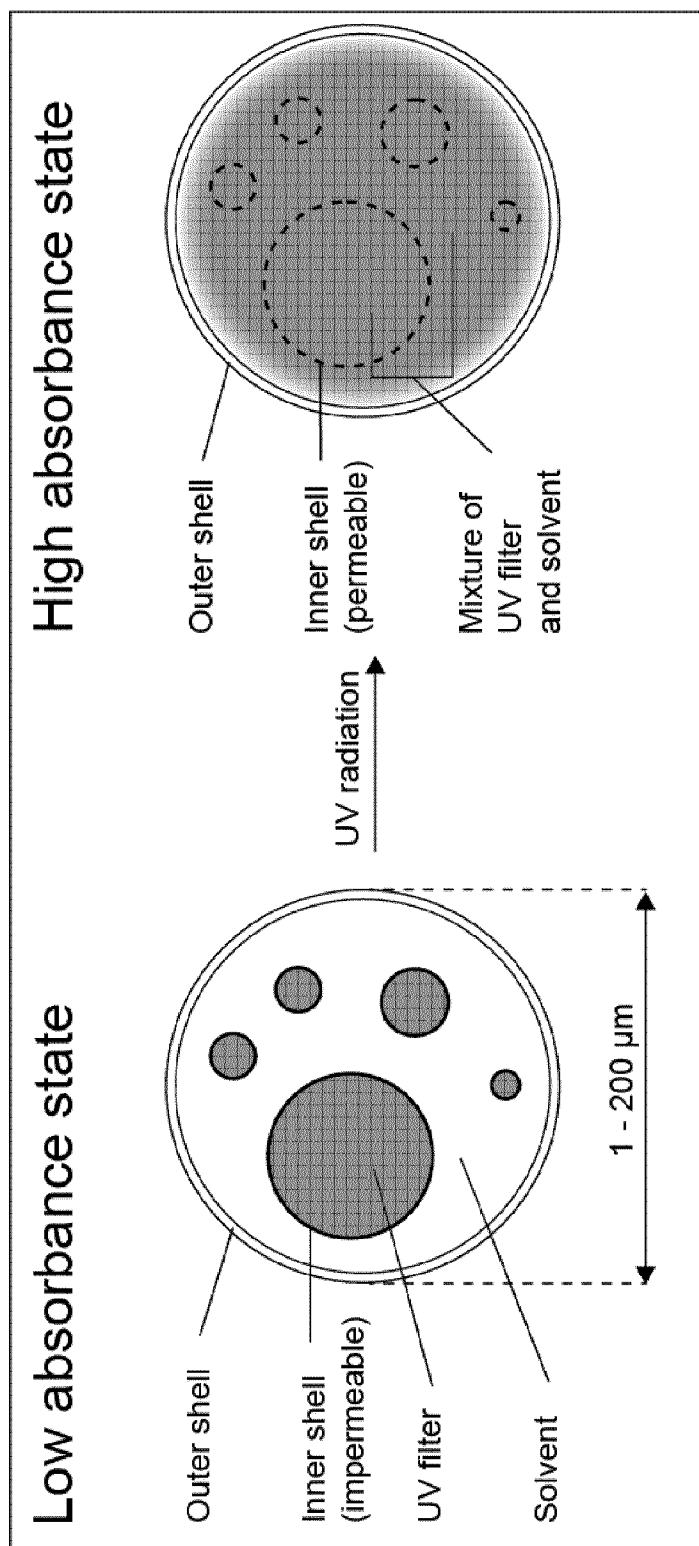


Fig. 4

Multiple layer microcapsules

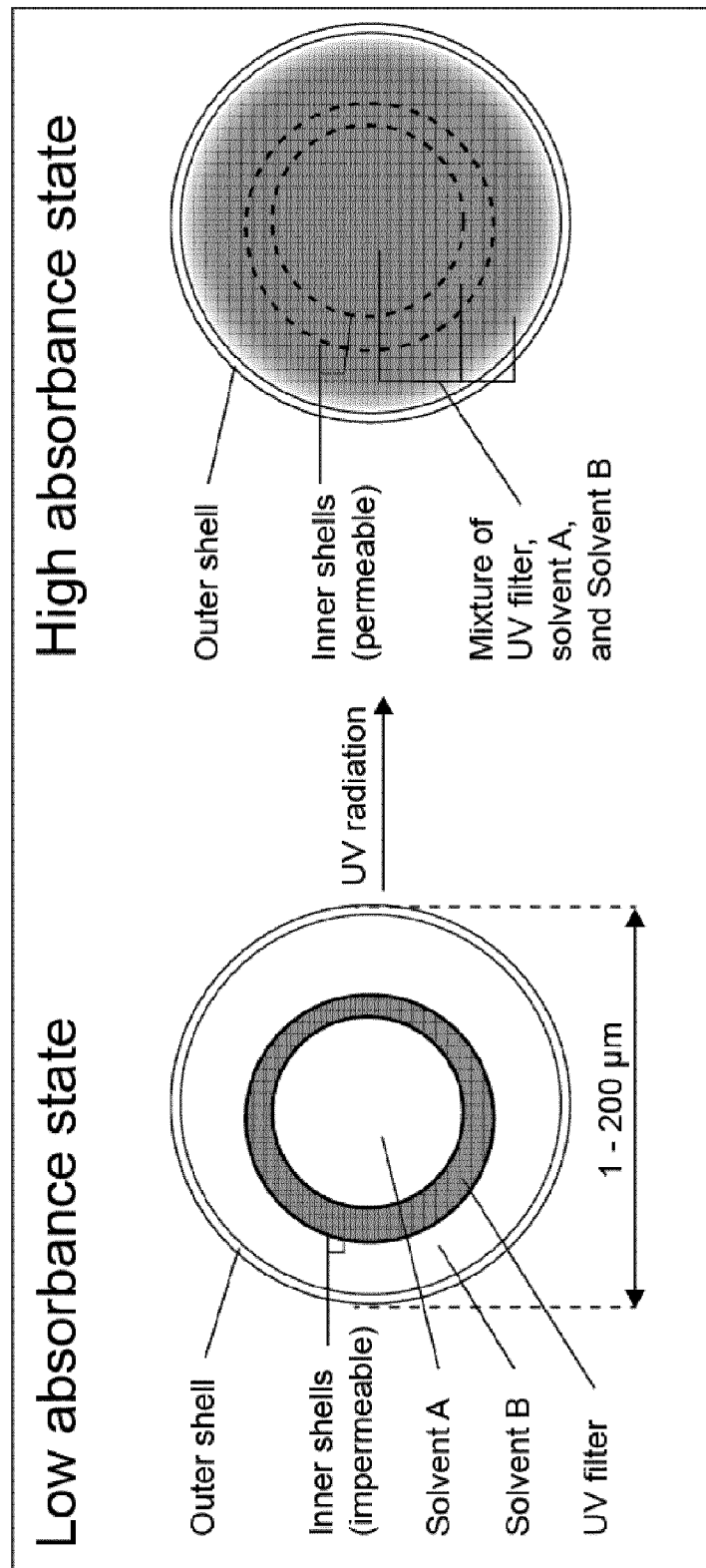


Fig. 5

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2012/051477

A. CLASSIFICATION OF SUBJECT MATTER
 INV. B01J13/22 A61Q17/04
 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 A61Q

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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"&" document member of the same patent family

Date of the actual completion of the international search

11 July 2012

Date of mailing of the international search report

19/07/2012

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/051477

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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