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(54) Title: A COSMETIC COMPOSITION INCLUDING AT LEAST ONE FLUOROPHORE COMPOUND

(57) Abstract: The present invention provides a cosmetic composition comprising: • a first fluorophore compound having an absorption spectrum; and • a second fluorophore compound having an emission spectrum overlapping the absorption spectrum of the first fluorophore compound, at least one of the two fluorophore compounds having luminescence enhanced by a proximity interaction effect with at least one metal, the metal and the fluorophore compound belonging to one and the same particle.



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A COSMETIC COMPOSITION INCLUDING AT LEAST ONE FLUOROPHORE
COMPOUND

The present invention relates to cosmetic compositions for application to the skin, the lips, hair,
5 or nails and more particularly but not exclusively to cosmetic compositions for lightening the skin or for modifying its tone.

Prior art

10 It is frequently observed that individuals with colored skin, or even dark skin, would like to lighten the color of their skin and to this end, they use cosmetic or dermatological compositions containing bleaching agents such as hydroquinone and its
15 derivatives, kojic acid and its derivatives, azelaic acid, arbutin and its derivatives, or alpha-hydroxyacids.

Some individuals also use such bleaching agents to attenuate or even to cause the disappearance of dyschromia of the skin occurring either with age or
20 following exposure to UV radiation, during pregnancy, or as a result of skin disease.

Such bleaching agents act by modifying the biological activity of melanocytes and by limiting pigmentation due to the formation of melanin.

25 This means that the effect of such bleaching agents only appear slowly after using them in an iterative and prolonged manner.

Further, since they only act on the endogenous biosynthesis of melanin, such bleaching agents cannot
30 modify the tone of the lightening.

Furthermore, some of those agents such as hydroquinone or its derivatives have proved to have a certain degree of cytotoxicity. Broadly, such bleaching agents induce phenomena of allergies or skin irritation
35 that can be severe.

It is also quite frequently observed that individuals who wish to lighten the color of their skin

or to attenuate dyschromias use cosmetic compositions that make the complexion uniform, giving it an immediate white appearance. Such compositions contain diffusing white pigments that provide them with opacity and the coverage necessary to obtain the desired effect.

However, that covering power creates opacity that makes the made-up skin lose its natural appearance, transparency, and clarity. In particular, it generates a grayish, lifeless effect.

Furthermore, technical solutions employing emissive compounds such as fluorescent organic, semi-organic, or inorganic molecules or materials in cosmetic compositions are limited by various effects rendering the lightening of the skin color barely perceptible.

Effects that may be mentioned are those due to intensities of emission under natural light excitation that are too weak because of their intrinsic molecular structures; effects due to photo-degradation of the fluorophores and to their chemical reactivity with the environment of the formulation, reducing the quantity of fluorescent substances in the compositions containing them; effects due to the phenomenon of absorption of wavelengths in the visible region dominating the phenomenon of emission and thus producing inappropriate colors when lightening the complexion; effects due to the limited amounts of filler of such emissive compounds in the organic, semi-organic or inorganic matrixes intended to protect them from their chemical and/or photo chemical interactions with their environment and resulting in emission intensities that are too low.

Thus, a genuine need exists for emissive materials to be available that emit light in the visible region after excitation by natural light, in which the intensity of emission is sufficiently high to render the lightening of the skin color by the cosmetic compositions containing them perceptible, and that have sufficient stability under natural illumination and in conjunction with the

ingredients of the cosmetic compositions in which they are contained.

A need also exists for such emissive materials to be sufficiently transparent to provide the skin onto which
5 said cosmetic compositions containing them are applied with a clear, non-opaque, natural appearance that does not provide too much coverage.

Furthermore, there is also a need for the effect of lightening of the skin color to be immediately
10 perceptible, and then to persist, if so desired, for one to a few days and for the tone to be capable of being modulated as a function of the various types of skin tones that are treated.

The problem of lightening the complexion constitutes
15 the subject matter of many publications.

Publication FR 2 778 561 proposes the use of optical brighteners, possibly in association with skin bleaching agents, UV screens, anti-wrinkle agents, and moisturizing agents. The chemical families of those optical
20 brighteners are more particularly those of stilbene, coumarin, oxazole, benzoxazole, and imidazole. More precisely, Tinopal SOP and Uvitex OB are proposed. However, the skin lightening effect is not entirely satisfactory, and cannot be used to modulate the tone as
25 much as would be liked as a function of various skin tones.

In addition, in general, organic optical brighteners are unstable in light, which results in a reduction in the lightening efficiency of cosmetic compositions
30 containing them. They also have a certain reactivity with the components of the cosmetic compositions, which denatures their molecular structure, thereby inducing a reduction in the fluorescence of the brightener and thus in the lightening effect.

35 The publication WO 01/43714 discloses polymeric particles, in particular based on starch or cellulose, doped with optical brighteners. The quantity by weight

of fluorescent agent in the matrix is limited by the solubility and matrix diffusion properties, and is around a value of 1.5%. The intensity of the fluorescence is limited thereby, along with the consequent lightening effect.

The publication FR 2 810 881 proposes lightening the skin color by applying a composition containing optical brighteners included in inorganic particles such as titanium oxide aluminas. Here again, the limited quantities of fluorescent active ingredients in the inorganic matrix renders the lightening effect barely perceptible.

The publication FR 2 857 254 proposes cosmetic compositions containing mineral microparticles having a high degree of porosity where the organic optical brightener is immobilized and thus protected from possible chemical reactions that would reduce the intensity of fluorescence. However, the concentration of brightener in such mineral matrixes remains relatively limited and the lightening effect is diminished.

To overcome this, publication FR 2 885 520 proposes cosmetic compositions containing a mixture of at least two photoluminescent agents that may be coated with a transparent matrix with a mean dimension of less than 100 nm [nanometer], such as the compounds Luminux Effect Blue A, Luminux Effect Red A, Luminux Effect Green A, sold by the supplier Honeywell. However, those photoluminescent agents have phosphorescence and weak fluorescence, which makes them luminescent in the dark and weakly so in daylight. The visibility of the skin color lightening effect is thus relatively small in daylight.

Another solution proposed by the publication FR 2 885 521 concerns cosmetic compositions containing photoluminescent nanoparticles comprising at least one rare earth with a mean dimension of less than 500 nm. However, it is known that rare earths have a coefficient

of extinction and a quantum yield that is low compared with organic fluorophores. Thus, the skin lightening effect remains relatively moderate.

The publication US 2007/0221884 proposes compositions containing silica particles into which nanoparticles of inorganic fluorophores such as ZnS, ZnCdS, CdZnS: Ag, etc. have been included. The inorganic fluorophores, with the exception of II/VI quantum dots (QD II/VI) such as those based on cadmium or tellurium, are known to be less fluorescent than organic fluorophores, which tends to reduce the intensity of the lightening effect. With QD II/VI, in addition, the inherent toxicity of the Cd²⁺ or Te³⁺ ions renders them impossible to use in cosmetic applications.

The solution proposed by the publication FR 2 873 021 employs cosmetic compositions containing fluorescent silicon nanoparticles, such as those sold by the supplier NanoSi Inc. The photostability of those fluorescent agents is improved along with their chemical stability, but the quantum yields for fluorescence are relatively low, causing the intensity of the desired effect to be barely perceptible.

The publication W000/72808 discloses the use of compositions containing inorganic fluorescent compounds in glass matrixes. The desired effect resides more in perceiving a reduction in the appearance of circles/dark lines rather than in skin lightening.

Alongside solutions aimed at overcoming problems of chemical and photonic stability of the fluorophores, another solution for enhancing the intensity of the radiation emitted by the fluorescent compounds is proposed in the publication FR 2 848 842 and relies on the presence in a cosmetic composition of at least one optical brightener and a fluorescent compound such that the emission wavelength of the optical brightener corresponds to the absorption wavelength of the fluorescent compound. The optical brighteners proposed

cannot of themselves produce a skin lightening effect and they are used in this context to supply radiative energy to the associated fluorescent compound. They fluoresce in the wavelength range 550 nm to 700 nm, i.e. in the orange and red range. This results in a lightening effect that is clearly insufficient to which an inappropriate orange-red color is added.

In order to overcome all of the problems mentioned above, the publications FR 2 848 821 and FR 2 848 822 propose cosmetic compositions containing colorizing agents and reflective particles with a color from pinky beige to orangey beige, characterized by a hue h between 50° and 70° and a saturation C in the range 20 to 50. That solution is limited because of the use of colorizing agents that absorb light to provide the desired hue. This results in dulling of the skin that cannot be compensated for or corrected by the reflective particles. For this reason, the luminosity of such compositions remains relatively low and the lightening effect is not entirely satisfactory.

Furthermore, it is common to use colorizing agents such as white opacifying mineral or organic fillers in order to attempt to lighten the skin color. However, they also create a grayish color effect that is particularly visible on dark skins, especially black colored. In order to partially compensate for this effect, the publication FR 2 872 032 proposes cosmetic compositions containing solid particles with a refractive index in the range 1.2 to 1.5 derived from cured elastomeric organopolysiloxanes, a liquid binder with a refractive index in the range 1.2 to 1.6, and a colorizing agent that can provide the composition with a color such that the hue h is in the range 40° to 70° and the saturation C is in the range 20 to 50. Although the skin color obtained after application of the compositions containing such ingredients is less dull than with those described in the publications FR 2 848 821 and FR

2 848 822, the lightening effect is still relatively difficult to notice and is hard to modulate.

The publication WO2009/003996 discloses the use of cosmetic compositions containing both particles of
5 titanium oxide with a dimension in the range 300 nm to 1000 nm and also biological bleaching agents such as vitamin B3 or its niacinamide and nicotine derivatives. That association produces an immediate bleaching effect provided by the titanium oxide particles, as well as a
10 long term effect due to the biological bleaching agents. However, here again, the skin color obtained owes more to an opacifying bleaching effect than to a luminous lightening of the complexion.

15 Summary

A need exists for further improving cosmetic compositions in order, for example, to lighten the skin, for example to enhance its reflectance in the
500 nm-600 nm, 600 nm-700 nm or 500 nm-700 nm region
20 and/or to modify the tone, or to produce novel makeup effects.

More generally, there is an interest in having available novel cosmetic compositions that, depending on the desired result, may be used for making up human
25 keratinous substrates, such as the skin, in particular of the body, hands, neck, face, and lips, and/or such as keratinous fibers, especially the eyelashes, eyebrows or hair of the head, for example, to provide immediate, long-lasting and modulatable lightening of the tone of
30 those keratinous substrates while retaining a natural appearance and/or to camouflage skin dyschromias.

Exemplary embodiments of the invention provide a cosmetic composition comprising:

- a first fluorophore compound, in particular having
35 an absorption spectrum in the ultraviolet or visible region; and

• a second fluorophore compound having an emission spectrum in the visible region overlapping the absorption spectrum of the first fluorophore compound, at least one of the two fluorophore compounds having luminescence enhanced by a proximity interaction effect with at least one metal, the metal and the fluorophore compound for which the fluorescence is enhanced being present in the same particle, i.e. one and the same particulate particle.

As an example, the invention allows the composition to absorb in a first wavelength range, especially in the blue and/or UV, and to re-emit by luminescence in a second wavelength range relatively far away from the first, especially in the red, which is not possible with a single fluorophore compound selected from the compounds in conventional use.

It has been shown to be of particular interest to absorb in the blue and emit in the red, since the skin does not generally benefit esthetically from being illuminated with a predominantly blue light, while its appearance can be augmented with a light that is predominantly red.

The invention also means that the intensity of the luminescence in the red may be enhanced by exploiting the excitation energy of the incident light in the blue.

The composition may comprise at least three different fluorophore compounds, as detailed below, at least two of said compounds possibly having fluorescence absorption and excitation spectra located in the visible and also re-emitting in the visible.

The first fluorophore compound may have increased luminescence within a first particulate material, namely that one and the same particle comprises the metal and the fluorophore.

The second fluorophore compound may have an increased luminescence in a second particulate material,

namely that one and the same particle comprises the metal and the fluorophore.

The composition may comprise a third fluorophore compound. The third fluorophore compound may have
5 enhanced luminescence within a third particulate material, namely one and the same particle comprises the metal and the fluorophore.

In the presence of three fluorophore compounds, they may be selected so that they have respective emission
10 spectra in the red, in the green, and in the blue, in order to generate by addition white light or substantially white light by addition. Fluorophore compounds that emit in the red may also emit in the green, if appropriate. Those emitting in the green may
15 also absorb in the blue if appropriate.

The emission spectrum for the first fluorophore compound may cover the range from 580 nm to 700 nm, preferably with a mid-height width for the emission curve of the first fluorophore compound in the range 580 nm to
20 700 nm.

The emission spectrum for the second fluorophore compound may be in the range 480 nm to 620 nm, preferably with a mid-height width for the emission curve of the second fluorophore compound in the range 480 nm to
25 620 nm.

The first fluorophore compound may have a mid-height emission curve width in the range 580 nm to 700 nm and an absorption curve in the visible taken at mid-height in the range 480 nm to 620 nm, the second fluorophore
30 compound having an emission curve taken at mid-height in the range 480 nm to 620 nm.

The coverage of the composition is preferably 70% or less, more preferably 65% or less, or 60%. Thus, the composition has little or no opacifying power and the
35 natural appearance of the skin is preserved.

The emission spectrum for the composition in the red may have an emission peak that substantially coincides

with the maximum peak of sensitivity in the red for the human eye according to the CIE.

All of the fluorophore compounds of the composition may be free of rare earths.

5 In other exemplary embodiments the invention provides a cosmetic treatment method in which a composition as defined above is applied to the skin.

10 The invention also provides a method of modifying the tone of the skin and/or for lightening the skin, in which a composition as defined above is applied to the skin, the covering power of the composition being 70% or less, more preferably 65%, still more preferably 60%.

15 In further exemplary embodiments, independently of or in combination with the above, the invention provides a method of lightening the complexion or of modulating the tone of the skin, in which a cosmetic composition comprising at least one particulate material within which a fluorophore has enhanced fluorescence, in particular particles with a nanometric metallic core and a coating
20 covering the core, said coating comprising at least one fluorescent molecule disposed at the surface of the coating or impregnating it and located at a distance from the metallic core that is sufficiently small to increase its fluorescence, is applied to the skin.

25 The term "modulating the tone" denotes a change in the color of the skin by means of a non opacifying composition or a composition that barely opacifies, in particular with a covering power of 70% or less, preferably 65%, more preferably 60%.

30 In further exemplary embodiments, independently of or in combination with the above, the invention provides a method of enhancing the reflectance of skin in the wavelength region in the range 600 nm to 700 nm, comprising the step consisting in applying to the skin a
35 cosmetic composition comprising at least two fluorophore compounds F1 and F2, characterized in that the fluorophore compound F1 emits fluorescent light in the

visible region such that the normalized emission curve for said fluorophore compound F1 and the relative luminous efficiency curve defined by the CIE overlap each other in the wavelength region in the range 600 nm to 700 nm; and in that the absorption curve for the fluorophore F1 and the emission curve for the fluorophore F2 overlap each other when irradiated with natural light.

The term "normalized curve" means a curve reduced to a scale of 0 to 100%.

10 In further exemplary embodiments, independently of or in combination with the above, the invention provides a method of enhancing the reflectance of skin in the wavelength region in the range 500 nm to 600 nm, the method comprising the step consisting in applying to the skin a cosmetic composition comprising at least two fluorophore compounds F3 and F4, and being characterized in that the fluorophore compound F4 emits fluorescent light in the visible region such that the normalized emission curve for the fluorophore compound F4 and the relative luminous efficiency curve defined by the CIE overlap each other in the wavelength region in the range 500 nm to 600 nm and in that the absorption curve for the fluorophore F4 and the emission curve for the fluorophore F3 overlap each other when irradiated with natural light.

25 In further exemplary embodiments, independently of or in combination with the above, the invention provides a method of enhancing the reflectance of skin in the wavelength region in the range 500 nm to 700 nm, comprising the step consisting in applying to the skin a cosmetic composition comprising at least three fluorophore compounds F5, F6, and F7, the method being characterized in that the fluorophore compound F5 emits fluorescent light in the visible region such that the normalized emission curve for the fluorophore compound F5 and the relative luminous efficiency curve defined by the CIE overlap each other in the wavelength region in the range 400 nm to 500 nm; in that the fluorophore compound

F6 emits fluorescent light in the visible region such that the normalized emission curve for said fluorophore compound F6 and the relative luminous efficiency curve defined by the CIE overlap each other in the wavelength region in the range 500 nm to 600 nm; in that the fluorophore compound F7 emits fluorescent light in the visible region such that the normalized emission curve for said fluorophore compound F7 and the relative luminous efficiency curve defined by the CIE overlap each other in the wavelength region in the range 600 nm to 700 nm; in that the absorption curve for the fluorophore F6 and the emission curve for the fluorophore F5 overlap each other; and in that the absorption curve for the fluorophore F7 and the emission curve for the fluorophore F6 overlap each other when irradiated with natural light.

Preferably and in general, when overlapping is desired between two spectra, for example as described above, an emission spectrum for a fluorophore compound and an absorption spectrum of another fluorophore compound or between an emission spectrum for a fluorophore compound and the relative luminous efficiency curve, the overlap between the curves is such that twice the common area of the two overlapping curves represents at least 20%, 30%, 40%, 50%, 60%, 70% or preferably 80% of the sum of the areas of each of said curves. This value is termed the degree of overlap. The mid-height width of the common area is, for example, more than 5 nm wide, or even more than 10, 20 or 30 nm wide.

The invention also pertains to a cosmetic composition per se, to implement one of the methods defined above.

The term "visible region" is assumed to be the range from 400 nm to 700 nm.

The relative luminous efficiency curve corresponds to the photopic vision curve for day vision as defined by the CIE on the site, <http://www.led-fr.net/efficacite-lumineuse-relative.htm>, given in Figure 6.

However, that curve could more preferably be replaced for $\lambda > 550$ nm by the curve R CIE 1964 XYZ CMFs, shown in Figure 7 after normalization.

Each of the fluorophore compounds F1 to F7 preferably has enhanced fluorescence in a particulate material, namely one and the same particle comprising the metal and the fluorophore.

Skin lightening

10 A composition of the invention may act to lighten the skin, as shown in the implementational examples. It should be understood that "skin lightening" means a modification of the reflectance of the made-up skin compared with bare skin, such that an observer would see
15 it as being lighter without it in any way losing its natural appearance.

The lightening may be observed if the overall reflectance of the made-up skin is greater than the reflectance of the skin that has not been made up. The
20 reflectance of a material denotes the percentage of light reflected by that material compared with that observed with a perfectly white reference material at each wavelength under consideration, in accordance with the definition customarily adopted by the skilled person.

25 Enhancement of the reflectance due to the composition implies that the reflectance spectrum of the made-up skin has, at least over one spectral window, reflectance values that are higher than the values observed in the same spectral window for skin that has
30 not been made up. That relative enhancement of the reflectance is at least 5%, preferably more than 10%.

Preferably, the composition of the invention enhances the reflectance of the skin in the range 600 nm-700 nm, preferably by at least 0.05, preferably
35 0.1, on a scale from 0 to 1, for at least one wavelength, and preferably for at least a 20 nm wide interval, or even 50 nm wide, in this 600 nm-700 nm range.

Skin lightening protocol

The reflectances may be measured before and after making up using an acquisition device such as that described in Figure 1 of application US 2003/0067545, comprising a sphere inside which several independent and non-apparent sources of white light are disposed so that the light reaching its aperture is as uniform as possible. The face of the individual whose color is to be measured is placed in that aperture and images are acquired using color cameras or digital photographic apparatus, the reflectance spectra being acquired using a spectroradiometer. Prior to image acquisition, the acquisition system is calibrated by placing colorimetric standard references in the field of the cameras, for example using the method described in US 6 362 849, the contents of which are herewith incorporated by reference.

The color measurements may, for example, be carried out in three regions of the face, for example a first region located on the forehead, a second region corresponding to the pouches under the eyes and a third region between the nose and the lips.

The color is measured before making up the skin that has been cleansed and after making up, for example 15 minutes after finishing it.

For the lightening measurement, the makeup compositions are applied directly onto the skin in the usual manner without previously depositing a base, in an amount of approximately 0.5 mg [milligram] to 1 mg per cm² [square centimeter], preferably in the range 0.7 mg/cm² to 0.8 mg/cm².

Preferably, the coverage of the composition is not too high, in order to retain a natural appearance for the makeup.

35

Measurement of coverage

Compositions that are liquid (at 25°C)

The term "liquid composition" means a composition of viscosity that can be measured. A liquid composition is capable of flowing under the effect of its own weight.

The coverage of the liquid compositions is measured
5 at a finished thickness of 50 μm [micrometer] for liquid compositions for application to the lips, especially liquid lipsticks, liquid lip glosses, and liquid lip balms, for nail polishes, eye shadows, liquid foundations, mascaras, and other liquid makeup products
10 not intended for application to the lips.

The composition is smoothed onto matt black and matt white contrast cards, for example with trade mark LENETA Form WP1 for the matt black card and LENETA 1A for the matt white card.

15 Application may be carried out with an automatic smoother.

The measurements are carried out on the compositions that have been smoothed on.

20 Compositions that are solid (at 25°C)

Solid compositions are those of viscosity that cannot be measured.

They may be compositions cast into sticks or powders, in the form of loose or pressed powders.

25 a) For solid powder compositions, loose or pressed, the composition is applied using the same contrast cards as above, coated with a transparent, slightly rough adhesive strip, for example of trade mark BLENDERM® from the supplier 3M with reference 15025, bonded to the
30 contrast cards via the adhesive face.

The composition is deposited onto the adhesive strip so as to obtain a uniform deposit of
 $0.5 \text{ mg/cm}^2 \pm 0.02 \text{ mg/cm}^2$.

35 It is possible to use a sponge loaded with the composition for deposition and mounted on a dispersing apparatus that makes pre-defined movements with the sponge. The sponge is, for example, a single-use sponge

of the "LANCÔME - Photogenic" type used on the pink side.

b) Stick compositions are melted, for example at 90°C, then smoothed in the liquid state onto matt black and matt white contrast cards, for example with the same references as above, but not covered with BLENDERM®. The smoothing bar is kept at the same temperature as the composition in order to avoid thermal shock.

Once melted, the stick compositions are then deposited with a thickness of 50 µm [micrometer].

10

Measurements and calculations

The reflectance spectra are acquired using a MINOLTA 3700-d spectrophotometer (diffuse measurement geometry/8° and D65/10° observation, specular mode excluded, small opening (CREISS)) on black and white backgrounds, the contrast cards possibly being covered with BLENDERM® as indicated above.

The spectra are expressed in colorimetric coordinates in CIELab76 space as defined by the Commission Internationale de l'Eclairage in accordance with recommendation 15:2004.

The contrast ratio, or coverage, is calculated by taking the arithmetic mean of Y on the black background divided by the mean value of Y on the white background multiplied by 100.

In order to preserve a natural appearance for the skin with the cosmetic compositions of the invention, the coverage values are preferably less than 70%, more preferably less than 65%, ideally less than 60%.

30

Choice of emission and absorption spectra

Figure 1 illustrates the overlap between the absorption spectrum A₁ of a first fluorophore compound of an example of a composition of the invention and the emission spectrum E₂ of another fluorophore compound of the composition, these fluorophore compounds both belonging, for example, to respective particulate

materials comprising a metal interacting with the fluorophore.

The overlap of spectra A_1 and E_2 may be such that twice the common area as represented by the gray common portion is at least 20% of the sum of the areas of spectra A_1 and E_2 , i.e. the degree of overlap is at least 20%, or more, e.g. at least 50%.

In one example, the mid-height of the emission spectrum E_1 of the first fluorophore compound is in the range 580 nm to 700 nm. The absorption spectrum A_1 is, for example, in the range 480 nm to 600 nm and the emission spectrum for the second fluorophore compound E_2 is in the range 480 nm to 600 nm.

When the composition comprises at least one third fluorophore compound, the emission spectrum E_3 thereof may overlap, for example with a degree of overlap of more than 0.2, 0.5 or more, with the absorption spectrum A_1 and the absorption spectrum A_3 of the third fluorophore compound may be offset from the spectrum A_2 , for example offset further towards shorter wavelengths, as illustrated in Figure 2. The emission spectrum E_3 may also overlap the absorption spectrum A_2 , for example with a degree of overlap of more than 0.2, 0.5 or more, as illustrated in Figure 3.

In order to enhance the reflectance of skin in the wavelength region in the range 600 nm to 700 nm, exemplary embodiments of the cosmetic composition may comprise at least two fluorophore compounds $F1$ and $F2$ characterized in that the fluorophore compound $F1$ emits fluorescent light in the visible region such that the normalized emission curve for said fluorophore compound $F1$ and the relative luminous efficiency curve defined by the CIE overlap each other in the wavelength region in the range 600 nm to 700 nm, for example with a degree of overlap of more than 0.2, 0.5 or more; and in that the absorption curve for the fluorophore $F1$ and the emission curve for the fluorophore $F2$ overlap each other under

natural light, for example with a degree of overlap of more than 0.2, or even 0.5 or more. The term "natural light" means light with the characteristics of the D₆₅ illuminant.

5 In order to enhance the reflectance of skin in the wavelength region in the range 500 nm to 600 nm, exemplary embodiments of the cosmetic composition may comprise at least two fluorophore compounds F3 and F4 characterized in that the fluorophore compound F4 emits
10 fluorescent light in the visible region such that the normalized emission curve for the fluorophore compound F4 and the relative luminous efficiency curve defined by the CIE overlap each other in the wavelength region in the range 500 nm to 600 nm, for example with a degree of
15 overlap of more than 0.2, 0.5 or more; and in that the absorption curve for the fluorophore F4 and the emission curve for the fluorophore F3 overlap each other under natural light, for example with a degree of overlap of more than 0.2, or even 0.5 or more.

20 In order to enhance the reflectance of skin in the wavelength region in the range 500 nm to 700 nm, exemplary embodiments of the cosmetic composition may comprise at least three fluorophore compounds F5, F6, and F7 characterized in that the fluorophore compound F5
25 emits fluorescent light in the visible region such that the normalized emission curve for the fluorophore compound F5 and the relative luminous efficiency curve defined by the CIE overlap each other in the wavelength region in the range 400 nm to 500 nm, for example with a
30 degree of overlap of more than 0.2, 0.5 or more; in that the fluorophore compound F6 emits fluorescent light in the visible region such that the normalized emission curve for said fluorophore compound F6 and the relative luminous efficiency curve defined by the CIE overlap each
35 other in the wavelength region in the range 500 nm to 600 nm; and in that the fluorophore compound F7 emits fluorescent light in the visible region such that the

normalized emission curve for the fluorophore compound F7 and the relative luminous efficiency curve defined by the CIE overlap each other in the wavelength region in the range 600 nm to 700 nm, for example with a degree of overlap of more than 0.2 or even 0.5 or more; in that the absorption curve for the fluorophore F6 and the emission curve for the fluorophore F5 overlap each other and in that the absorption curve for the fluorophore F7 and the emission curve for the fluorophore F6 overlap each other under natural light, for example with a degree of overlap of more than 0.2, or even 0.5 or more.

PARTICULATE MATERIALS COMPRISING AT LEAST ONE FLUOROPHORE INTERACTING WITH AT LEAST ONE METAL

The term "fluorophore compound" should be understood to mean a fluorescent compound.

The absorption spectrum of such a compound is that leading to excitation giving rise to fluorescence.

The total weight content of fluorophore compounds in the composition of the invention may lie in the range 0.0001% to 90% by weight. In general, the particulate material may be in the form of particles that may have a spherical or flake shape.

The particulate material comprises at least one fluorophore and at least one metal, preferably a noble metal, and has a structure preferably corresponding to structures (I) and (II) described below. The enhanced fluorescence refers to the work by R.R. Chance, J. Chem. Phys. 1974, 60, 2744 and K.H. Drexhage, J. Lumin 1970, 1, 693 and in accordance with the invention encompasses MEF (*metal-enhanced fluorescence*) fluorescence as described in the publication "Metal-Enhanced Fluorescence", Chris D. Geddes and Joseph R. Lakowicz, Journal of Fluorescence, Vol 12, No 2, June 2002 and the publication "Plasmonic Enhancement of Molecular Fluorescence", N.J. Halas, Nano Lett. 2007, 7, 2, 496 to 501. MEF fluorescence is also occasionally termed SPCF (Surface

plasmon coupled fluorescence) or RDE (Radiative decay engineering).

It is possible for interaction to occur between the fluorophore and the metal in the particulate material because the distance between the two is sufficiently small, for example less than 300 nm, preferably less than 200 nm, more preferably less than 100 nm, or even 50 nm to 40 nm, or more preferably in the range 2 nm to 30 nm.

The invention is not limited to the particulate material structures (I) and (II) illustrated below and encompasses variations of these structures as well as other structures capable of producing amplification linked, for example, to a plasmonic resonance effect. As an example, the metal may be directly coated with a layer of a fluorophore compound. The metal and the fluorophore may also both be contained in a matrix. A particulate material of the present invention may also be constituted by an aggregate of at least two different materials, each possibly comprising a metal and a fluorophore interacting with the metal, for example.

The metals suitable for use in enhancing the luminescence of the fluorophore comprise, for example, one or more metals selected from the group constituted by the following metals: aluminum (Al), palladium (Pd), platinum (Pt), silver (Ag), copper (Cu), gold (Au), zinc (Zn) and alloys thereof. Preferably, the metal of the plasmonic particles is selected from the following metals: silver, aluminum, zinc, and gold and alloys thereof. Alloys of a plurality of metals may be stoichiometric or non-stoichiometric. When a plurality of metals is used, they may constitute a continuous metal phase such as an alloy, i.e. a continuous phase in which the metals are no longer dissociable, or a discontinuous phase of metals.

The metallic surface may have a variety of shapes such as spherical, cylindrical, cubic, conical, ovoid, polyhedral, with four to six faces, such as a perfect or

truncated tetrahedron, a perfect or truncated cube, or a flake, especially an elliptical, triangular, pyramidal, or polyhedral flake. They may be smooth or rough.

Preferably, the composition of the invention
5 comprises one or more particulate materials with structure (I) or (II) as defined below, with a mean dimension given by the D_{50} distribution in the range 10 nm to 1 micrometer, preferably in the range 30 nm to 500 nm.

In one exemplary embodiment, the composition of the
10 invention may thus comprise particulate materials with structure (I) or (II), in which the porosity of the outer shell is such that the pore size is in the range 1 nm to 50 nm, and the specific surface area is more than 500 m²/g [square meter/gram].

15 The cosmetic composition may comprise at least three fluorophore and metal materials, preferably each with structure (I) or (II), such that at least three fluorescence emissions are produced in the blue, green, and red in order to obtain a white or near white color.

20 F1, F2, F3, F4, F5, F6, and F7 described above may each be present in a structure of particulate materials (I) or (II) as defined below.

In general, irrespective of the structure of the particulate material, the particulate fluorophore
25 compound or compounds may be selected from any one of the fluorescent compounds described below, and more particularly from those listed for portion B and in Examples 1 to 14 below. When the composition contains a fluorophore compound, for example in the free state or
30 within a metal-free particulate material, the fluorophore may be any fluorophore, for example selected from those listed for portion B and in Examples 1 to 14.

Structure (I), as illustrated in Figure 4, comprises or is constituted by **three portions A, B and C**, in a
35 specific organization such that portion A is enveloped by portion C with a thickness of 1 nm to 100 nm and such that portion B is outside portion A and inside portion C,

optionally being bonded by covalent bonding to the chemical functions of portion C.

Structure (II), as illustrated in Figure 5, comprises or is constituted by **four portions D, E, C, and B** having a specific organization such that portion D is enveloped by portion E with a thickness of 1 nm to 100 nm, the ensemble obtained D+E itself being enveloped by portion C with a thickness of 1 nm to 100 nm and portion B being outside the ensemble D+E and inside portion C, possibly being bonded thereto by covalent bonding.

Portion A comprises or is even constituted by a metal particle, the metal being selected from group G_1 below, with a dimension in the range 3 nm to 500 nm in any one of the three axes in space, of shape that may be spherical, cylindrical, ovoid, conical, polyhedral, with four to ten faces, such as a perfect or truncated tetrahedron, a perfect or truncated cube (as described by Y. Xia, Science, 2002, 298, 5601, 2176 - 2179), a rectangular parallelepiped, an octagonal cylinder (as described by Y. Xia, Angew. Chem. Int. Ed., 2009, 48, 60 - 103), or a perfect or truncated octahedron (as described by P. Yang, Angew. Chem. Int. Ed., 2006, 45, 4597 - 4601; S. Schultz, J. Chem. Phys. 116, 15, 6755 - 6759).

The group G_1 is, for example, constituted by silver, gold, platinum, copper, aluminum, palladium, zinc, nickel, or one of their alloys.

The constitutive particles of portion A are preferably selected from the group constituted by the metals silver, gold, zinc, preferably silver, gold, and more preferably silver.

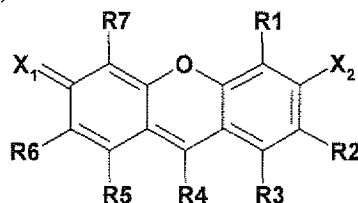
They are preferably spherical, cylindrical, pyramidal, or ovoid in shape, preferably spherical or ovoid; and more preferably spherical.

They are preferably in the range 3 nm to 300 nm in dimension; preferably in the range 3 nm to 160 nm; more

preferably in the range 30 nm to 80 nm for gold, or in the range 30 nm to 200 nm for silver. More preferably in the range 30 nm to 120 nm for silver.

Portion B comprises or is even constituted by at least one fluorophore independently selected from the list in the European Cosmetic Directive's FDA list: "Fluorescent Whitening Agent, Encyclopedia of Chemical Technology", Kirk-Othmer, 4th 11:227 - 241, 1994; group G₄ is constituted by compounds belonging to the following chemical families: xanthenes, benzo[a]xanthenes, benzo[b]xanthenes, benzo[c]xanthenes, coumarins, benzocoumarins, phenoxazines, benzo[a]phenoxazines, benzo[b]phenoxazines, benzo[c]phenoxazines, phenothiazines, benzo[b]thiazines, benzo[c]thiazines, naphthalimides, naphtholactams, lactamimides, quinacridones, epindolines, thio-epindolines, phthalimides, oxazolones, benzotriazoles, diphenylmaleimides, dibenzofurans, pyrimidines, triazines, 1,3,5-triazin-2-yl derivatives, pyrazines, triazoles, methines, distyrylbenzenes, distyrylbiphenyls, divinylstilbenes, triazinylaminostilbenes, stilbenyl-2H-triazoles, benzoxazoles, benzofurans, benzimidazoles, 1,3-diphenyl-2-pyrazolines, diketopyrrolopyrroles (EP-A-0 133 156, US 4 585 878, WO-98/25927, WO-03/064558, WO-04/009710, WO-05/005571), perylenes, perylene monoimides and 4,4-difluoro-4-bora-3a,4a-diaza-indacene.

a- Fluorophores from the xanthenes family are represented by the formula (F-I):



(F-I) where:

• X₁ represents an oxygen atom; an N-Z₁, N⁺Z₁Z₂ radical;

- X_2 represents a hydroxy radical; an NZ_1Z_2 radical;
- Z_1 , Z_2 , independently of each other, represent a radical selected from the group Gp_1 constituted by a hydrogen atom; a linear or branched C_1 - C_8 alkyl, optionally interrupted by one or more oxygen atoms, and optionally substituted with one or more radicals selected from the group constituted by a OR_8 radical, a NR_9R_{10} radical, a carboxy radical, a COOM radical, a thiol radical, a cyano radical, a halogen, a sulfonic radical, a $CONR_9R_{10}$ carboxamido radical, a $SO_2NR_9R_{10}$ sulfonamido radical; an aryl radical optionally substituted with one or more radicals selected from the group Gp_4 ; a heteroaryl radical optionally substituted with one or more radicals selected from the group Gp_4 ;
- The C_1 - C_8 alkyl chain as defined above may be interrupted by one or more oxygen atoms;
- Z_1 and Z_2 together with the nitrogen atom to which they are attached may form a saturated or unsaturated heterocycle containing 5 to 7 members, optionally substituted with one or more radicals selected from the group Gp_2 constituted by halogen atoms; amino; (di) (C_1 - C_4) alkylamino; hydroxy; carboxy; carboxamido; (C_1 - C_2)alkoxy radicals; C_1 - C_4 alkyl radicals optionally substituted with one or more hydroxy, amino, (di)-alkylamino, alkoxy, carboxy, or sulfonyl radicals; the cycle containing neither a peroxide bond nor diazo or nitroso radicals;
- X_1 (respectively X_2) may optionally be connected to R_6 and/or to R_7 (respectively to R_1 or R_2), to together form a saturated or unsaturated, possibly cationic carbocycle or a heterocycle containing 5 to 6 members such as, for example, a cyclohexyl, cyclohexenyl, cyclopentyl, cyclopentenyl, piperidiny, dehydropiperidiny, or pyrrolidinyl cycle, wherein the associated anion or mixture of anions is selected from the group constituted by a halide such as chloride, bromide, fluoride, or iodide, a hydroxide, a sulfate, a

hydrogenosulfate, an alkylsulfate wherein the alkyl portion, linear or branched, is C₁-C₆, such as the methylsulfate or ethylsulfate ion; carbonates and hydrogenocarbonates; carboxylic acid salts such as the formate, acetate, citrate, tartrate or oxalate; alkylsulfonates wherein the alkyl portion, linear or branched, is C₁-C₆, such as the methylsulfonate ion; arylsulfonates wherein the aryl portion, preferably phenyl, is optionally substituted with one or more C₁-C₄ alkyl radicals such as 4-toluylsulfonate, for example;

• R₁, R₂, R₃, R₅, R₆, R₇, which may be identical or different, represent a radical selected from the group Gp₃ constituted by a hydrogen atom; a halogen, a C₁-C₄ alkyl optionally substituted with one or more radicals selected from the group constituted by a OR₈ radical, a SR₈ radical, a NR₉R₁₀ radical, a carboxy radical, a sulfonic radical, a CONR₉R₁₀ carboxamido radical, a SO₂NR₉R₁₀ sulfonamido radical; a carboxy radical; a cyano radical, a carboxamido radical (RCONH-); a (C₁-C₄) alkylsulfonyl (SO₂R) radical; an alkylsulfonamido ((C₁-C₄) alkyl SO₂NH-) radical; a (-SO₃H) sulfonic radical; a C₁-C₄ thioether radical; a (C₁-C₄) alkylsulfoxide (-SOR) radical; an aminosulfonyl (NH₂-SO₂-) radical; a hydroxy radical; a C₁-C₄ alkoxy radical; a thioether radical; a C₂-C₄ hydroxyalkoxy radical; a NR₁₃R₁₄ radical; an aryl radical optionally substituted with one or more radicals selected from the group Gp₄; a heteroaryl radical optionally substituted with one or more radicals selected from the group Gp₄; or a cationic aza-heteroaryl radical optionally substituted with one or more radicals selected from the group Gp₄;

• R₅ and R₆ may form a saturated or unsaturated carbocycle or a heterocycle containing 6 members optionally substituted with one or more radicals selected from the group Gp₂;

• R₄ represents a hydrogen, halogen; cyano; trifluoromethyl; linear or branched C₂-C₈ alkyl; linear or

branched C₁-C₈ alkenyl; or linear or branched C₂-C₈ alkynyl radical; aryl optionally substituted with one or more radicals selected from group Gp₄; heteroaryl optionally substituted with one or more radicals selected from group Gp₄; naphthyl optionally substituted with one or more radicals selected from group Gp₄;

• R₈, R₉ and R₁₀, which may be identical or different, represent a hydrogen atom; or a linear or branched C₁-C₄ radical optionally substituted with one or more radicals selected from the group constituted by a hydroxy, a C₁-C₂ alkoxy, a CONR₁₁R₁₂ carboxamido, or a SO₂R₁₁ sulfonyl radical;

• R₁₁ and R₁₂, which may be identical or different, represent a hydrogen atom or a linear or branched C₁-C₄ alkyl radical optionally substituted with one or more hydroxy, C₁-C₂alkoxy;

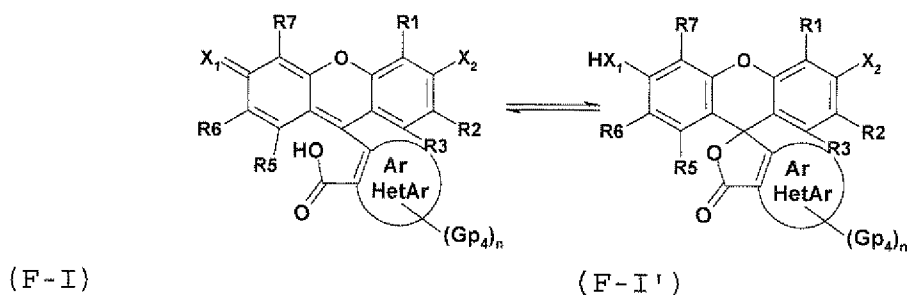
• The group Gp₄ is constituted by a halogen; cyano; hydroxy; C₁-C₄ alkoxy; carboxy; carboxamido; alkyl(C₁-C₄)sulfonyl (-SO₂alkyl) optionally substituted with a sulfonic (-SO₃H) group; a sulfonate SO₃M' where M' represents a lithium, sodium or potassium ion, sulfate (-OSO₃H); alkylsulfoxide (-SO-alkyl); alkylsulfonamido (alkyl(C₁-C₄)SO₂NH-); N₁₃R₁₄; nitro; phenyl optionally substituted; or a C₁-C₄ alkyl group optionally substituted with one or more radicals selected from hydroxy, C₁-C₄ alkoxy, carboxy, carboxamido, alkyl(C₁-C₄)sulfonyl, sulfonic, alkylsulfoxide, alkylsulfonamido and NR₁₃R₁₄; and possibly a salt thereof, and their solvates;

• R₁₃ and R₁₄ independently of each other represent a radical selected from the group Gp₁. Together with the nitrogen atom carrying them, they may form a cycle containing 5 to 7 members; and

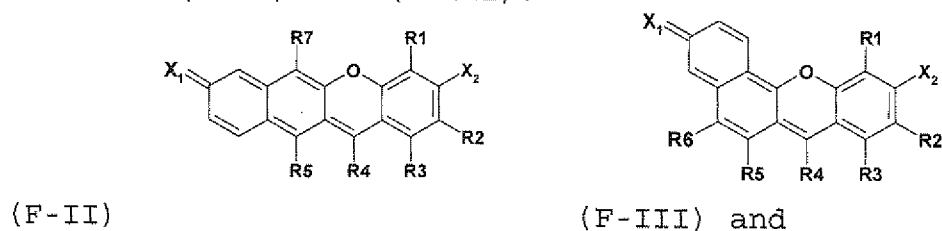
• M represents a lithium, sodium, potassium, calcium, magnesium, ammonium cation, which is mono, di, tri or tetra-substituted with a C₁-C₈ alkyl or C₂-C₄ hydroxyalkyl.

Particular compounds with formula (F-I) may sometimes be represented by their isomeric forms in accordance with the formula (F-I'), where n represents an integer from 0 to 4.

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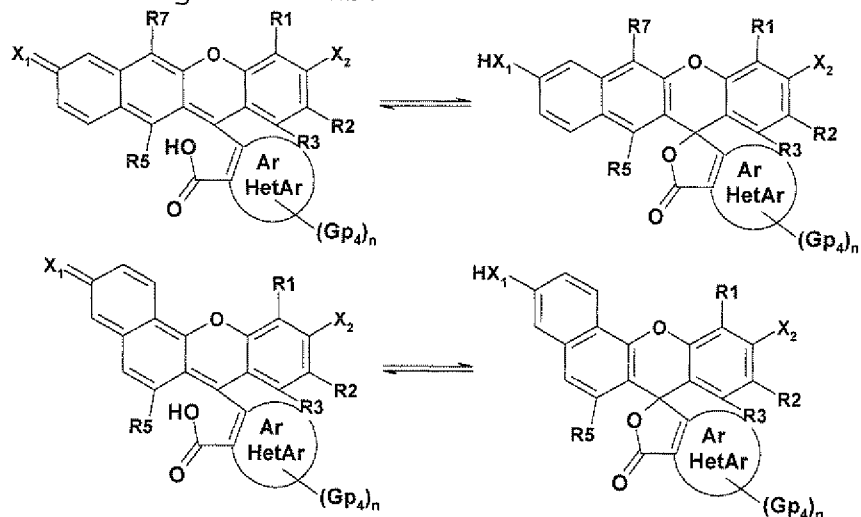


b- Fluorophores from the benzo[b]xanthenes and benzo[c]xanthenes family are respectively represented by formulas (F-II) and (F-III):



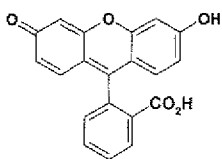
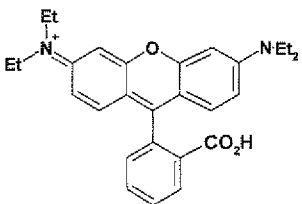
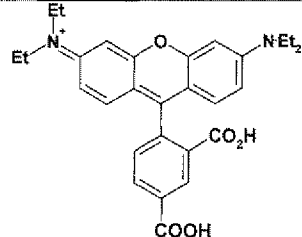
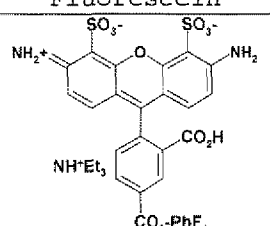
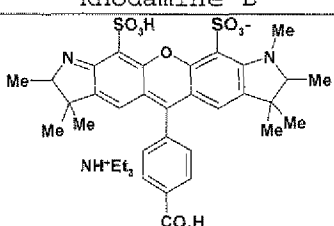
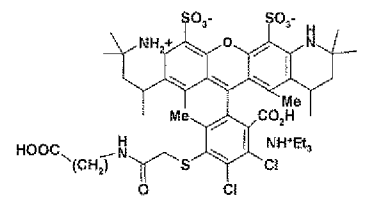
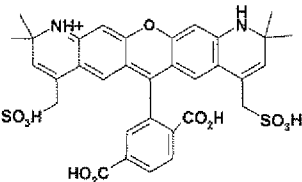
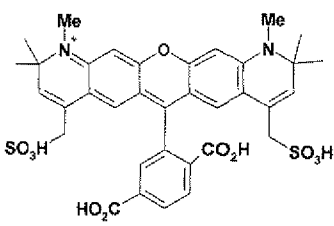
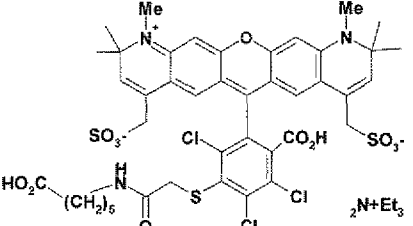
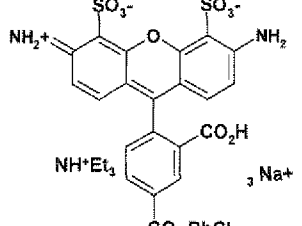
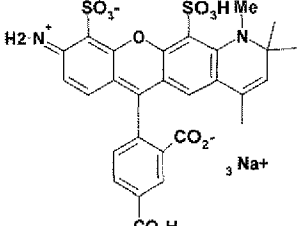
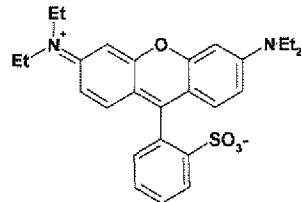
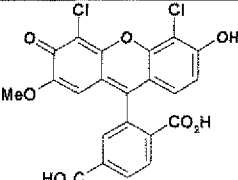
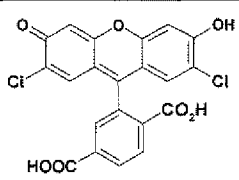
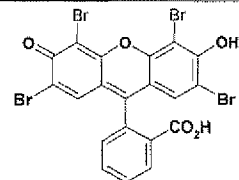
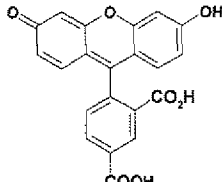
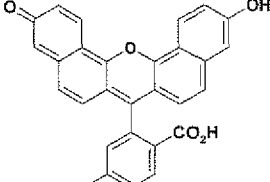
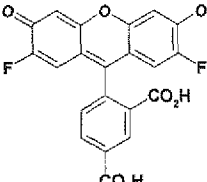
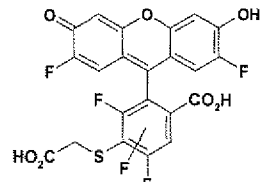
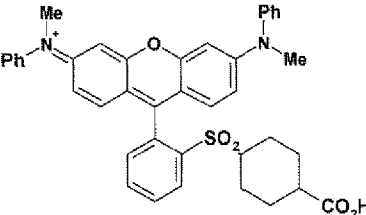
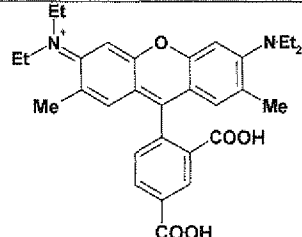
their isomeric forms in a representation analogous to that of (F-I) $\rightleftharpoons$ (F-I').

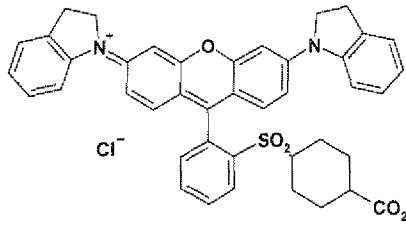
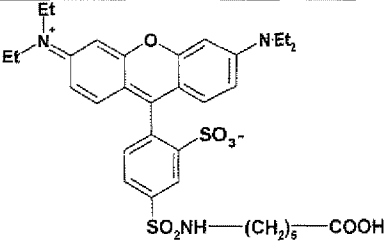
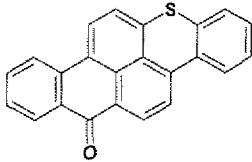
As an example, these isomeric forms are represented by the following formulas:



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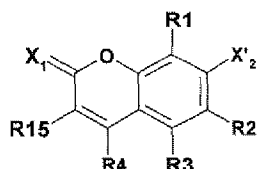
Preferred compounds with formula (F-I):

		
Fluorescein	Rhodamine B	
		
Alexa Fluor 488		
		
		
		
		
		

		 Solvent Orange 63
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c- Fluorophores from the coumarin family are respectively represented by the formulas (F-III) [400 nm - 500 nm] region:

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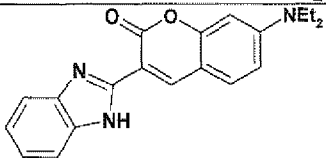
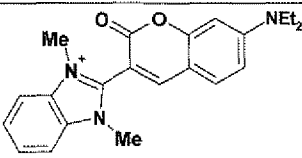
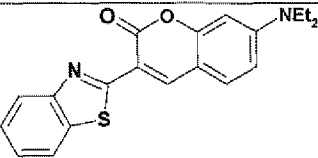
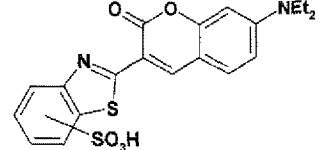
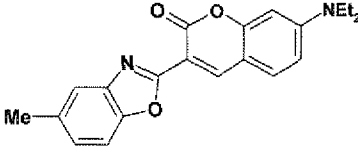
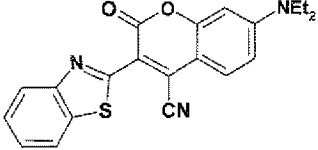
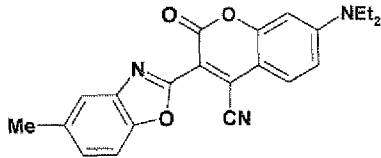
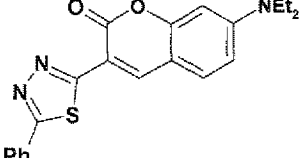
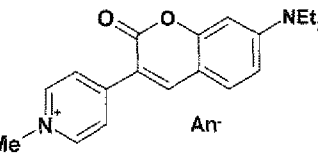
(F-III) where: R_{15} is defined by the same radicals as for R_1 ;

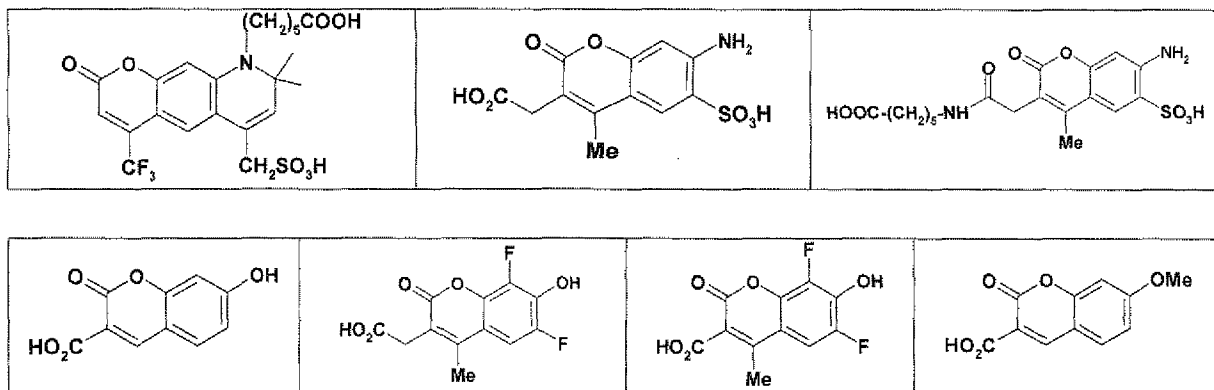
• X'_2 represents a hydroxy radical; a C_1 - C_2 alkoxy radical; or a NZ_1Z_2 radical provided that Z_1 and Z_2 do not together represent a hydrogen atom; and

• X'_2 and R_2 may together form a cycle containing 5 to 6 members, possibly unsaturated and optionally substituted with a radical from group Gp3.

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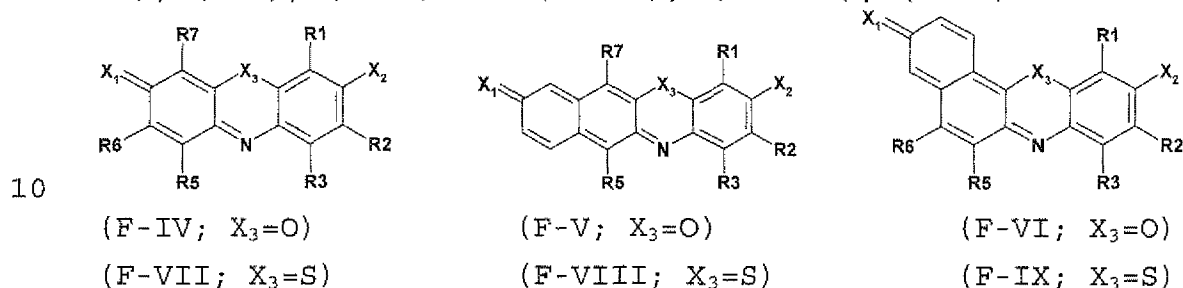
Preferred compounds with formula (F-III):



where An⁻ denotes a cosmetically acceptable anion.

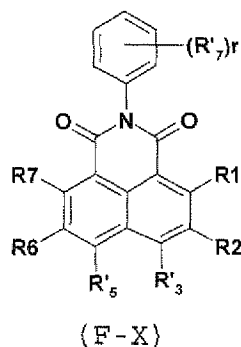
- 5 d- Fluorophores from the phenoxazines, benzo[b]phenoxazines, benzo[c]phenoxazines and phenothiazines, benzo[b]thiazines, benzo[c]thiazines family are respectively represented by the formulas (F-IV), (F-V), (F-VI) and (F-VII), (F-VIII), (F-IX)



Preferred compounds with formula (F-IV) and (F-VII):



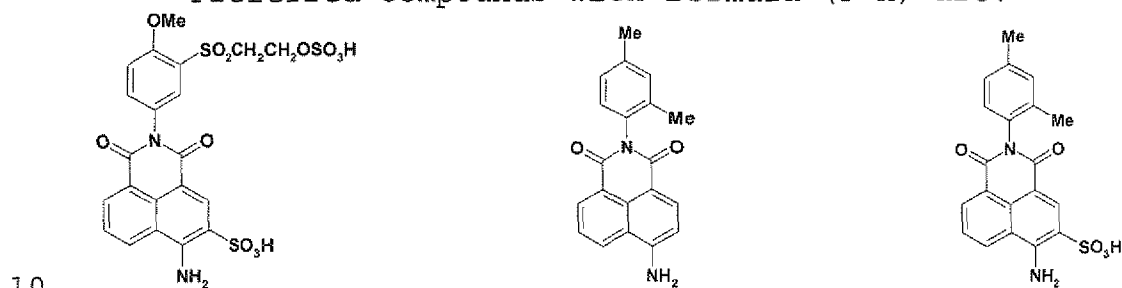
- 15 e- Fluorophores from the naphthalimides family are represented by the formula (F-X):



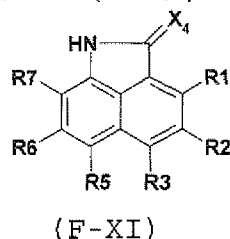
where:

- R'7 represents a radical selected from the group Gp₄;
- R'₃ and R'₅ represent radicals such as those defined for R₃ and R₅, and may possibly form a lactam cycle wherein the nitrogen atom is optionally substituted with a Z₁ group; and
- r represents an integer in the range 0 to 5.

Preferred compounds with formula (F-X) are:

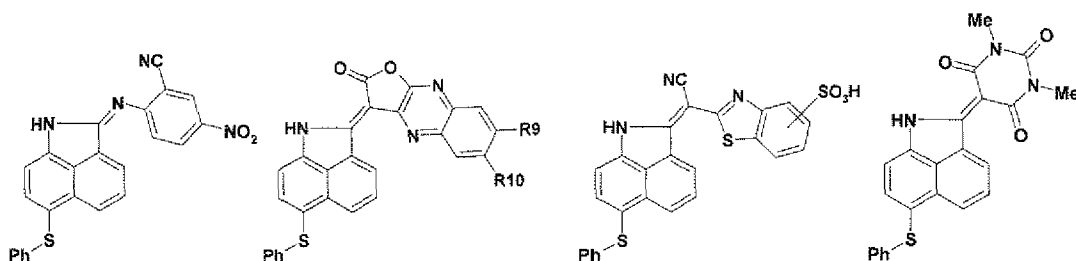


f- Fluorophores from the naphtholactams family are represented by the formula (F-XI):



- 15 where X₄ represents a radical such as that defined for X₁; a heterocyclic radical; a C₁-C₄ alkyl radical optionally substituted with one or more radicals selected from hydroxy, C₁-C₄ alkoxy, cyano; carboxy, carboxamido, (C₁-C₄) alkylsulfonyl, sulfonic, alkylsulfoxide,
- 20 alkylsulfonamide; aryl radicals optionally substituted with one or more radicals selected from group Gp₄; a heteroaryl radical optionally substituted with one or more radicals selected from group Gp₄.

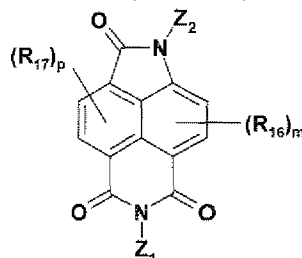
Preferred compounds with formula (F-XI) are:



where R_9 and R_{10} independently of each other designate a hydrogen atom, a C_1 - C_8 alkyl radical or a C_1 - C_6 alkoxy radical.

5

f- Fluorophores from the lactamimides family are represented by the formula (F-XII):



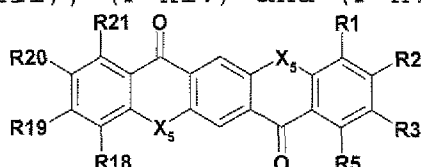
(F-XII) where R_{16} and R_{17} represent radicals such as those defined for radical R_1 ;

10

$\cdot$ $\underline{m}$ and $\underline{p}$ represent integers in the range 0 to 2.

g- Fluorophores from the quinacridone, epindoline and thio-epindoline family are respectively represented by the formulas (F-XIII), (F-XIV) and (F-XV):

15



(F-XIII) $X_5 = N-Z_1$ (F-XIV) $X_5 = O$ (F-XV) $X_5 = S$

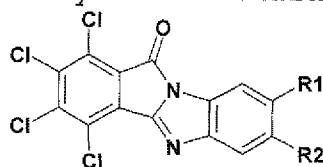
where X_5 represents an oxygen atom, sulfur atom or a $N-Z_1$ group;

$\cdot$ R_{18} , R_{19} , R_{20} , and R_{21} represent radicals such as those defined for radical R_1 .

20

Compounds derived from quinacridone that may emit white are described in WO-04/039805.

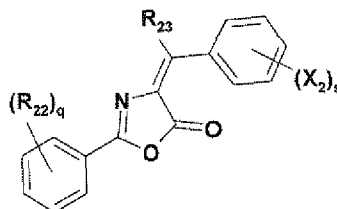
h- Fluorophores from the phthalimides family are preferably represented by the formula (F-XV):



(F-XV)

5

i- Fluorophores from the oxazolones family are preferably represented by the formula (F-XVI):



(F-XVI)

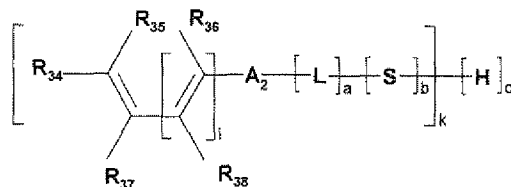
10 where:

- R_{22} and R_{23} independently of each other represent a radical selected from the group Gp_4 ; and
- s represents an integer in the range 0 to 5.

15 j- Fluorophores from the benzotriazoles family are described in the publications WO-03/105538 and EP-2004053111.

20 k- Fluorophores from the pyrimidines, triazine, triazoles, pyrazines, dibenzofurans family are described in the publications WO-04/039786, EP-2004/050146, WO-05/023960, EP-2004/052984, EP-2005/051731, EP-05/103497, EP-05/104599.

25 l- Fluorophores from the stilbenes family are represented by the formula (F-XVII):



(F-XVII)

where:

- i represents an integer equal to 0 to 1;
- k represents an integer equal to 1 to 2;
- a, b, and c represent integers equal to 0 to 1;

5 and

- such that $(a,b,c,k) = (0,0,1,1); (0,0,0,2), (1,0,0,1), (1,0,0,2), (1,1,0,2), \text{ or } (1,1,1,1).$

10 · R_{34} and A_2 represent an aryl radical optionally substituted with one or more radicals selected from the group Gp_5 ; an aromatic heterocyclic radical optionally substituted with one or more radicals selected from the group Gp_5 ; or a cationic aromatic heterocyclic radical optionally substituted with one or more radicals selected from the group Gp_5 ;

15 · The group Gp_5 is constituted by a hydrogen atom; a linear or branched C_1 - C_4 alkyl radical optionally substituted with one or more radicals selected from the group constituted by an OR_8 , SR_8 , NR_9R_{10} , carboxy, sulfonic, carboxamido $CONR_9R_{10}$, and sulfonamido $SO_2NR_9R_{10}$ radical; a $-CH=CH-CN$ radical; a $-CH=CH-CO_2R_8$ radical; a $-CH=CH-Ar$ radical where Ar represents an aryl group optionally substituted with a nitrile; a carboxy radical; a alkoxy carbonyl C_1 - C_3 radical; a cyano radical; a halogen radical; a $(RCONH-)$ carboxamido radical; a (C_1-C_4) alkylsulfonyl (SO_2R) radical; a alkylsulfonamido (C_1-C_4) alkyl SO_2NH- radical; a $(-SO_3H)$ sulfonic radical; a sulfonate radical $(-SO_3M)$, where M represents a sodium, potassium, or lithium ion); a C_1 - C_4 thioether radical; a (C_1-C_4) alkyl sulfoxide $(-SOR)$ radical; an aminosulfonyl radical (NH_2-SO_2-) ; a hydroxy radical; a C_1 - C_4 alkoxy radical; a C_2 - C_4 hydroxyalkoxy radical; a $NR_{39}R_{40}$ radical; an aryl radical optionally substituted with one or more radicals selected from the group Gp_4 ; a heteroaryl radical such as 1,2,3-triazole, 1,2,4-triazole, benzotriazole, benzoxazole, pyrazole, pyrazoline, pyrazolidine, indazole, imidazole, pyrrole, indole, pyrrolidine, indoline, oxadiazole, said radical possibly being

35

substituted with one or more radicals selected from the group Gp₄;

• R₃₉ and R₄₀ independently of each other represent a radical selected from the group Gp₁ and in particular a triazinyl group optionally substituted with a radical
5 selected from the group Gp₆ constituted by a C₁-C₄ alkoxy radical; NR₄₁R₄₂; C₁-C₄ alkyl optionally substituted with one or more radicals selected from hydroxy, C₁-C₄ alkoxy, carboxy, carboxamido, (C₁-C₄) alkyl sulfonyl, sulfonic,
10 alkylsulfoxide, alkylsulfonamido or NR₄₃R₄₄ radicals;

• R₃₉ and R₄₀ may together form a carbocycle or heterocycle containing 5 to 7 members with the nitrogen atom carrying them;

• R₄₁, R₄₂, R₄₃ and R₄₄ independently of each other
15 represent a radical selected from the group Gp₁;

• R₄₁ and R₄₂ on the one hand, R₄₃ and R₄₄ on the other hand may together form a carbocycle or heterocycle containing 5 to 7 members with the nitrogen atom that carries them such as a pyrrolidine, morpholine, or
20 thiomorpholine cycle, as non-limiting examples;

• R₃₅, R₃₆, R₃₇ and R₃₈ independently of each other represent a hydrogen radical; C₁-C₈ alkyl optionally substituted with one or more radicals selected from the group constituted by a OR₈ radical, a carboxy radical, a
25 sulfonic radical wherein the carbonaceous chain may possibly be interrupted by one or more oxygen atoms; carboxy; cyano;

• R₃₅ and R₃₆ (where i=1) or R₃₅ and R₃₇ (where i=0) may be connected together to form a heterocycle containing 5
30 members selected from furan, thiophene, pyrrole; or a carbocycle containing 6 to 10 members selected from aryl, naphthyl;

• R₃₄ and R₃₇ may be connected together to form a heterocycle selected from benzofuran, benzothiophene,
35 indole, azaindole;

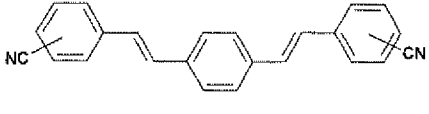
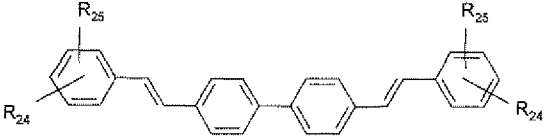
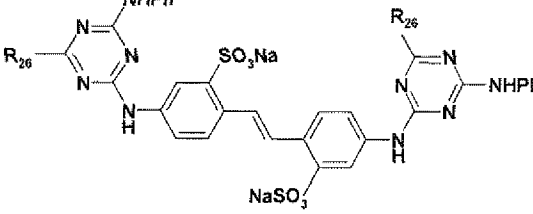
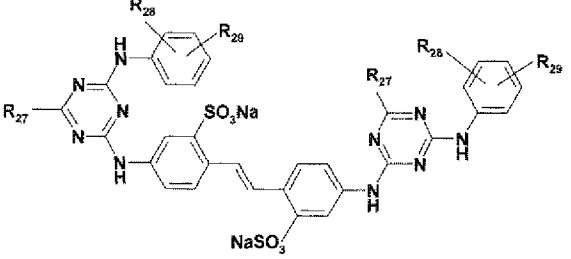
• L represents a linear or branched C₂-C₁₀ alkyl radical, the carbon chain of which may possibly be

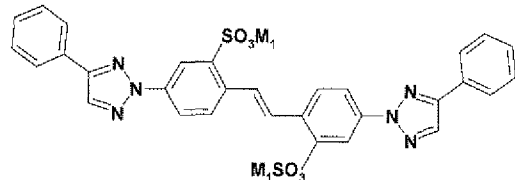
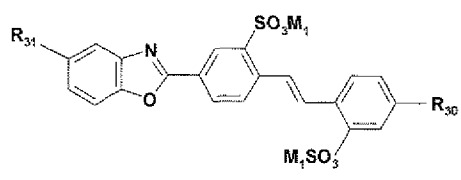
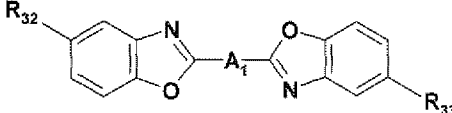
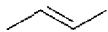
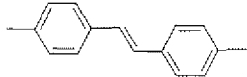
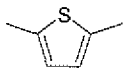
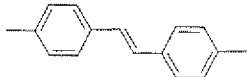
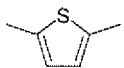
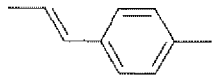
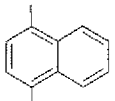
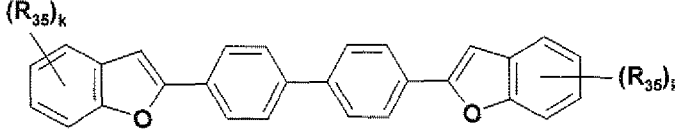
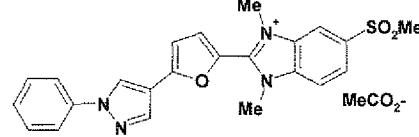
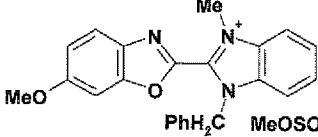
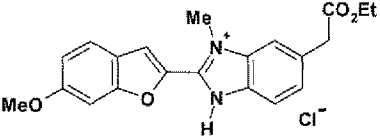
interrupted by at least one oxygen atom, optionally substituted with a C₂-C₈ alkoxy radical; or a (di) (C₂-C₈) alkylamino radical; and

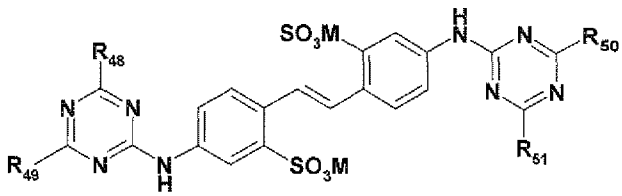
- R₃₄ and A₂, independently of each other, preferably
 5 represent a phenyl, naphthyl, pyridine, pyrimidine, imidazole, pyrazole, pyrrole, triazole, benzoxazole, benzimidazole, indole, azaindole, oxazolium, thiazolium, pyridinium, pyrimidinium, imidazolium, benzimidazolium, pyrazolium, pyrrolium, triazolium, oxazolium or
 10 thiazolium radical.

Preferred derivatives that may be mentioned are those of styrylstilbene, triazinostilbene, hydroxycoumarin, aminocoumarin, oxazole, benzoxazole, imidazole, triazole, pyrazoline, pyrene and porphyrin;

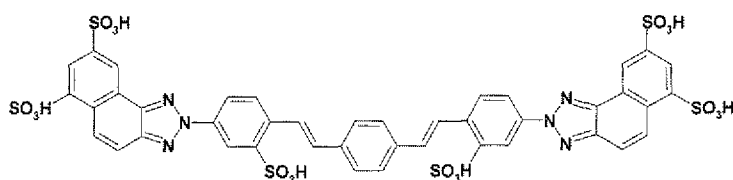
- 15 The following compounds illustrate preferred but non-limiting examples of this family:

			
Position (2,3), (2,4), (3,3), (3,4), (4,4).	(R ₂₄ , R ₂₅) = (SO ₃ Na (3), Cl (4)); (OMe (2), H); (SO ₃ Na (2), H).		
			
R ₂₆ = OMe, NHMe, NH ₂ Et, NH-CH ₂ -CH ₂ OH, NH(CH ₃)(CH ₂ -CH ₂ -OH), N-morpholinyl, NHPH,	R ₂₇	R ₂₈ (position)	R ₂₉ (position)
	NH-CH ₂ -CH ₂ OH	SO ₃ Na (3)	H
	N-(CH ₂ -CH ₂ OH) ₂	SO ₃ Na (3)	H
	N-(CH ₂ -CH ₂ OH) ₂	SO ₃ Na (4)	H
	N-(CH ₂ -CH ₂ OH) ₂	SO ₃ Na (2)	SO ₃ Na (5)
	N-(CH ₂ CH(OH)CH ₃) ₂	SO ₃ Na (4)	H
	N(CH ₃)(CH ₂ CH ₂ OH)	SO ₃ Na (4)	H
NEt ₂	SO ₃ Na (2)	SO ₃ Na (5)	

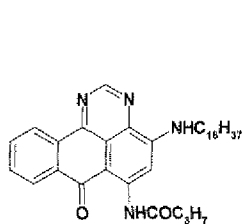
			N-morpholinyl N(CH ₂ CO ₂ Na) ₂	SO ₃ Na (2) SO ₃ Na (4)	SO ₃ Na (5) H			
								
M ₁ = Na, K			(R ₃₀ , R ₃₁) = (Me, COOMe) (H, methyloxadiazole)					
								
R ₃₂	R ₃₃	A ₁	R ₃₂	R ₃₃	A ₁			
Me	Me		H	H				
H	H		Me	H				
t-Bu	t-Bu		Me	Me				
H	H							
								
R ₃₅ = SO ₃ Na k=1, 2								
								

				
R ₄₈	R ₄₉	R ₅₀	R ₅₁	M
Amino	-N-(CH ₂ CH ₂ OH) ₂	Amino	-N-(CH ₂ CH ₂ OH) ₂	Na
Amino	-N-Et(CH ₂ CH ₂ OH)	Amino	-N-Et(CH ₂ CH ₂ OH)	Na
Amino	-NH-CH ₂ -COONa	Amino	-NH-CH ₂ -COONa	Na
Amino	-N-Me(CH ₂ CH ₂ OH)	Amino	-N-Me(CH ₂ CH ₂ OH)	Na
Amino	-N-morpholino	Amino	-N-morpholino	Na
Amino	-NMe-CH ₂ -COONa	Amino	-NMe-CH ₂ -COONa	Na
Amino	-NH-(CH ₂ CH ₂ OMe)	Amino	-NH-(CH ₂ CH ₂ OMe)	Na
-N-(CH ₂ CH ₂ OH) ₂	-N-(CH ₂ CH ₂ OH) ₂	-N-(CH ₂ CH ₂ OH) ₂	-N-(CH ₂ CH ₂ OH) ₂	Na
-NH-(CH ₂ CH ₂ OH)	-NH-(CH ₂ CH ₂ OH)	-NH-(CH ₂ CH ₂ OH)	-NH-(CH ₂ CH ₂ OH)	Na
-NH-(CH ₂ CH ₂ OH)	-N-morpholino	-NH-(CH ₂ CH ₂ OH)	-N-morpholino	NH ₄ ⁺
Amino	-NH-(CH ₂ CH ₂ CO ₂ Na)	Amino	-NH-(CH ₂ CH ₂ COONa)	Na
Amino	-NH-(CH ₂ CH ₂ OH)	Amino	-NH-(CH ₂ CH ₂ OH)	Na
Amino	-N-morpholino	Amino	-NH-(CH ₂ CH ₂ OMe)	Na
Amino	-N-morpholino	Amino	-NH-(CH ₂ CH ₂ OH)	Na
Amino	-N-morpholino	Amino	-NH-CH ₂ -COOH	Na

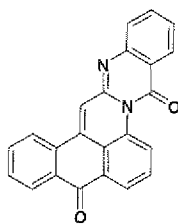
The following fluorophores are also preferred:



C.I. Direct Yellow 96

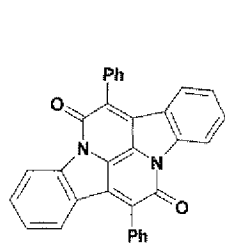


Fluorol 242

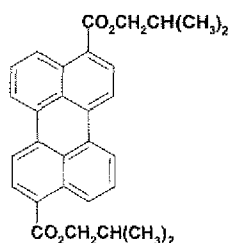


Dispersed Yellow 77

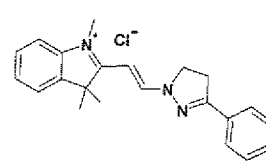
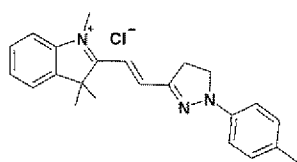
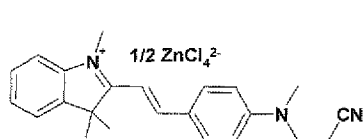
5



Ciba Lake



Solvent Green 5



	R ₄₅	R ₄₆	R ₄₇
	H	H	SO ₂ Me
	H	H	SO ₂ CH ₂ CH ₂ OH
	H	H	SO ₂ CH ₂ CH ₂ SO ₃ Na
	H	H	CO ₂ Na
	Cl	Me	SO ₂ CH ₂ CH ₂ SO ₃ Na
	H	H	-(CH ₂) ₂ -N ⁺ H Me ₂ , H ₂ PO ₃ ⁻
	H	H	-(CH ₂) ₂ -N ⁺ H Me ₂ , HCOO ⁻
	H	H	-CH ₂ -CHMe-N ⁺ H Me ₂ , CH ₃ CH(OH)COO ⁻

	H	H	$-(\text{CH}_2)_2-\text{CONH}-(\text{CH}_2)_3-\text{N}^+\text{HMe}_2, \text{Cl}^-$
	H	H	$-(\text{CH}_2)_2-\text{O}-\text{CHMe}-\text{CH}_2-\text{N}^+\text{HMe}_2, \text{Cl}^-$
	H	H	$\text{NH}-(\text{CH}_2)_3-\text{N}^+\text{Me}_3, \text{CH}_3\text{OSO}_3^-$
	H	H	$-\text{NH}-(\text{CH}_2)_3-\text{N}^+\text{Me}_2(\text{CH}_2\text{CH}_2\text{OH}), \text{COO}^-$

Preferred compounds for B are:

• DC Orange n° 4: Sodium 4-[(2-hydroxy-1-naphthyl)azo]benzenesulfonate;

5 • DC Red n° 31: Calcium bis[3-hydroxy-4-(phenylazo)-2-naphthoate];

• DC Red n° 6 and DC Red 7 (Ca salt of DC Red 6): Disodium 3-hydroxy-4-[(4-methyl-2-sulfonatophenyl)azo]-2-naphthoate;

10 • DC Red n° 34: Calcium 3-hydroxy-4-[(1-sulfonato-2-naphthyl)azo]-2-naphthoate;

• FDC Yellow n° 6: Disodium 6-hydroxy-5-[(3-sulfonatophenyl)azo]naphthalene-2-sulfonate;

15 • FDC Red n° 40: Disodium 6-hydroxy-5-[(2-methoxy-4-sulfonato-m-tolyl)azo]naphthalene-2-sulfonate;

• DC Red n° 33: Disodium 5-amino-4-hydroxy-3-(phenylazo)naphthalene-2,7-disulfonate;

• FDC Yellow n° 5: Trisodium 5-hydroxy-1-(4-sulfophenyl)-4-(4-sulfophenylazo)pyrazole-3-carboxylate;

20 • DC Red n° 17: 1-(4-(phenylazo)phenylazo)-2-naphthol;

• FDC Green n° 3: Dihydrogen (ethyl)[4-[4-[ethyl(3-sulfonatobenzyl)amino](4-hydroxy-2-sulfonatobenzhydrylidene)cyclohexa-2,5-dien-1-ylidene](3-sulfonatobenzyl)ammonium, disodium salt;

25 • FDC Blue n° 1: Dihydrogen (ethyl)[4-[4-[ethyl(3-sulfonatobenzyl)]amino]-2'-sulfonatobenzhydrylidene]cyclohexa-2,5-dien-1-ylidene](3-sulfonatobenzyl)ammonium, disodium salt;

30 • DC Yellow n° 7 and 8: Disodium 2-(3-oxo-6-oxidoxanthen-9-yl)benzoate;

• DC Orange N° 5: Disodium 2-(4,5-dibromo-6-oxido-3-oxoxanthen-9-yl)benzoate;

- DC Red n° 21: 2-(2,4,5,7-tetrabromo-6-oxido-3-oxoxanthen-9-yl)benzoic acid;
- DC Red n° 22: Disodium 2-(2,4,5,7-tetrabromo-6-oxido-3-oxoxanthen-9-yl)benzoate;
- 5 • DC Red n° 27: 3,4,5,6-tetrachloro-2-(1,4,5,8-tetrabromo-6-hydroxy-3-oxoxanthen-9-yl)benzoic acid;
- DC Red n° 28: 3,4,5,6-tetrachloro-2-(1,4,5,8-tetrabromo-6-hydroxy-3-oxoxanthen-9-yl)benzoate sodium;
- DC Yellow n° 11: 1,3-isobenzofurandione, reaction
- 10 product with methylquinoline and quinolone;
- DC Yellow n° 10: 1H-Indene-1,3(2H)-dione, 2-(2-quinolinyl)-, sulfonated, sodium salts;
- DC Green n° 8: Trisodium 8-hydroxypyrene-1,3,6-trisulfonate;
- 15 • DC Violet n° 2: 1-hydroxy-4-(p-toluidino)anthraquinone;
- DC Violet n° 2: Sodium 4-[(9,10-dihydro-4-hydroxy-9,10-dioxo-1-anthryl)amino]toluene-3-sulfonate;
- DC Green n° 6: 1,4-bis(p-tolylamino)anthraquinone;
- 20 • DC Green n° 5: Disodium 2,2'-(9,10-dioxoanthracene-1,4-diyl-diimino)bis(5-methylsulfonate);
- DC Red n° 30: 6-chloro-2-(6-chloro-4-methyl-3-oxobenzo[b]thien-2(3H)-ylidene)-4-methylbenzo[b]thiophene-3(2H)-one;
- 25 • Carminic acid;
- Disodium 4,4'-bis[(4-anilino-6-morpholino-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulfonate;
- Butyl 4-({4-[4-(butoxycarbonyl)phenyl]amino}-6-[(3-{1,3,3,3-tetramethyl-1-[(trimethylsilyl)oxy]disiloxanyl}propyl)amino]-1,3,5-triazin-2-yl}amino)benzoate;
- 30 • Methyl 1-methyl-4-[(methylphenylhydrazono)methyl]pyridinium sulfate
- 2-[[4-(dimethylamino)phenyl]azo]-1,3-dimethyl-1H-imidazolium chloride;
- 35

- (1E)-1-{4-[bis(2-hydroxyethyl)amino]benzylidene}-2,3-dihydro-1H-indolizinium chloride;
- Berberine;
- 5 Alexa Fluor 488
- Trisodium 5-hydroxy-1-(4-sulfophenyl)-4-(4-sulfophenylazo)pyrazole-3-carboxylate;
- 2,7-bis-(2-carboxyethyl)-5-carboxyfluorescein (BDECF);
- 10 • Rhod-2, tripotassium;
- Cascade Blue, trisodium;
- Cascade Yellow;
- 7-hydroxy-4-methylcoumarin;
- 5-ROX, 1-[[[2',3',6',7',12',13',16',17'-
- 15 octahydro-3-oxospiro[isobenzofuran-1(3H),9'-[1H,5H,9H,11H,15H]xantheno[2,3,4-ij:5,6,7-i'j']diquinolizin]-5(or 6)-yl]carboxylic acid;
- CY-3 cyanine;
- Benzophenone-1 (UVINUL 400); Benzophenone-2
- 20 (UVINUL D-50); Benzophenone-3 (UVINUL M-40); Benzophenone-4 (UVINUL MS-40); Benzophenone-8 (SPECTRA SORB UV-24); Methoxycinnamate (BERNEL HYDRO); Ethyl dihydroxypropyl-PABA (AMERSCREEN P); Glyceryl PABA (NIPA GMPA); Homosalate (KEMESTER HMS); Methyl Anthranilate
- 25 (SUNAROME UVA); Octocrylene (UVINUL N-539); Octyl dimethyl PABA (PABA);
- Octyl dimethoxycinnamate (PARSIL MCX); Octyl salicylate (SUNAROME WMO); p-amino benzoic acid (PABA); 2-phenylbenzimidazole-5-sulfonic acid (EUSOLEX 232);
- 30 Triethanolamine salicylate (SUNAROME W); 3-(4-methylbenzylidene)-camphor (UNSOLEX 6300); Benzophenone-6 (UVINUL D-49); Benzophenone-12 (UVINUL 408); 4-isopropylidibenzoylmethane (EUSOLEX 8020); Butyl methoxydibenzoylmethane (PARSOL1789); Etocrylene (UVINUL
- 35 N-35);
- TINOPAL OB (CIBA, 2,5-thiophenediylbis(5-ter-butyl-1,3-benzoxazole);

- TINOPAL ABP-Z (CIBA); TINOPAL NFW;
- TINOPAL CBS-X (CIBA, sodium 2,2'-([1,1'-biphenyl]-4,4'-diyldivinylene)bis(benzenesulfonate));
- TINOPAL DMA-X (CIBA, disodium 4,4'-bis[(4-anilino-6-morpholino-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulfonate;
- TINOPAL MSP (CIBA, hexasodium 2,2'-[vinylenebis[(3-sulfonato-4,1-phenylene)imino(6-morpholino-1,3,5-triazine-4,2-diyl)imino]]bis(benzene-1,4-disulfonate);
- TINOPAL NP Slurry (CIBA);
- TINOPAL SFP (CIBA, hexasodium 2,2'-[vinylenebis[(3-sulfonato-4,1-phenylene)imino(6-diethylamino)-1,3,5-triazine-4,2-diyl)imino]]bis(benzene-1,4-disulfonate);
- XYMARA Marker Blue SF2A (CIBA);
- UVITEX NFW (CIBA, disodium 4,4'-bis(2-sulfostyryl)-biphenyl);
- UVITEX OB (CIBA, 2,5-thiophenediylbis(5-ter-butyl-1,3-benzoxazole); and
- LEUCOPHOR BSB (CLARIANT); HOSTALUX ETBN (CLARIANT); LEUCOPHOR PC (CLARIANT); LEUCOPHOR N (CLARIANT); LEUCOPHOR UO (CLARIANT); LEUCOPHOR FTS (CLARIANT); LEUCOPHOR SAC (CLARIANT); LEUCOPHOR A (CLARIANT); LEUCOPHOR VW (CLARIANT); LEUCOPHOR LS (CLARIANT).

More preferably:

- TINOPAL CBS-X (CIBA, sodium 2,2'-([1,1'-biphenyl]-4,4'-diyldivinylene)bis(benzenesulfonate));
- TINOPAL DMA-X (CIBA, disodium 4,4'-bis[(4-anilino-6-morpholino-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulfonate;
- UVITEX OB (CIBA, 2,5-thiophenediylbis(5-ter-butyl-1,3-benzoxazole);
- DC Red n° 33: Disodium 5-amino-4-hydroxy-3-(phenylazo)naphthalene-2,7-disulfonate;

- FDC Green n° 3: Dihydrogen (ethyl) [4-[4-[ethyl(3-sulfonatobenzyl)amino](4-hydroxy-2-sulfonatobenzhydrylidene)cyclohexa-2,5-dien-1-ylidene](3-sulfonatobenzyl)ammonium, disodium salt;
- 5 • DC Red n°28: sodium 3,4,5,6-tetrachloro-2-(1,4,5,8-tetrabromo-6-hydroxy-3-oxoxanthene-9-yl)benzoate;
 DC Red n°27: 3,4,5,6-tetrachloro-2-(1,4,5,8-tetrabromo-6-hydroxy-3-oxoxanthene-9-yl)benzoic acid;
 DC Red n° 21: 2-(2,4,5,7-tetrabromo-6-oxido-3-oxoxanthene-9-yl)benzoic acid
- 10 • DC Orange N° 5: Disodium 2-(4,5-dibromo-6-oxido-3-oxoxanthene-9-yl)benzoate;
- DC Yellow n° 7 to 8: Disodium 2-(3-oxo-6-oxidoxanthene-9-yl)benzoate;
- 15 FDC Yellow n° 6: Disodium 6-hydroxy-5-[(3-sulfonatophenyl)azo]naphthalene-2-sulfonate
 FDC Yellow n° 5: Trisodium 5-hydroxy-1-(4-sulfophenyl)-4-(4-sulfophenylazo)pyrazole-3-carboxylate;
- FDC Blue n° 1: Dihydrogen (ethyl) [4-[4-[ethyl(3-sulfonatobenzyl)]amino]-2'-sulfonatobenzhydrylidene]cyclohexa-2,5-dien-1-ylidene](3-sulfonatobenzyl)ammonium, disodium salt;
- 20 Alexa Fluor 488
 • Butyl 4-({4-{[4-(butoxycarbonyl)phenyl]amino}-6-[(3-{1,3,3,3-tetramethyl-1-[(trimethylsilyl)oxy]disiloxanyl}propyl)amino]-1,3,5-triazin-2-yl}amino)benzoate;
- 25 • Trisodium 5-hydroxy-1-(4-sulfophenyl)-4-(4-sulfophenylazo)pyrazole-3-carboxylate;
- 30 • 2,7-bis-(2-carboxyethyl)-5-carboxyfluorescein (BDECF);
 • Rhod-2, tripotassium;
- Cascade Blue, trisodium;
- Cascade Yellow;
- 35 • 7-hydroxy-4-methylcoumarin;
- Trisodium 5-hydroxy-1-(4-sulfophenyl)-4-(4-sulfophenylazo)pyrazole-3-carboxylate;

- 5-ROX, 1-[[[2',3',6',7',12',13',16',17'-octahydro-3-oxospiro[isobenzofuran-1(3H),9'-[1H,5H,9H,11H,15H]xantheno[2,3,4-ij:5,6,7-i'j']diquinolizin]-5(or 6)-yl]carboxylic acid; and
- 5 • CY-3 cyanine.

And still more preferably:

- 7-hydroxy-4-methylcoumarin;
- Trisodium 5-hydroxy-1-(4-sulfophenyl)-4-(4-sulfophenylazo)pyrazole-3-carboxylate;
- 10 DC Red n°28: sodium 3,4,5,6-tetrachloro-2-(1,4,5,8-tetrabromo-6-hydroxy-3-oxoxanthen-9-yl)benzoate
- DC Red n°27: 3,4,5,6-tetrachloro-2-(1,4,5,8-tetrabromo-6-hydroxy-3-oxoxanthen-9-yl)benzoic acid;
- 15 DC Red n° 21: 2-(2,4,5,7-tetrabromo-6-oxido-3-oxoxanthen-9-yl)benzoic acid
- DC Orange N° 5: Disodium 2-(4,5-dibromo-6-oxido-3-oxoxanthen-9-yl)benzoate;
- FDC Blue n° 1: Dihydrogen (ethyl)[4-[4-[ethyl(3-sulfonatobenzyl)]amino]-2'-sulfonatobenzhydrylidene]cyclohexa-2,5-dien-1-ylidene](3-sulfonatobenzyl)ammonium, disodium salt;
- 20 • DC Red n° 33: Disodium 5-amino-4-hydroxy-3-(phenylazo)naphthalene-2,7-disulfonate;
- 25 FDC Yellow n° 6: Disodium 6-hydroxy-5-[(3-sulfonatophenyl)azo]naphthalene-2-sulfonate
- FDC Yellow n° 5: Trisodium 5-hydroxy-1-(4-sulfophenyl)-4-(4-sulfophenylazo)pyrazole-3-carboxylate;
- 30 • TINOPAL CBS-X (CIBA, sodium 2,2'-([1,1'-biphenyl]-4,4'-diyldivinylene)bis(benzenesulfonate));
- TINOPAL DMA-X (CIBA, disodium 4,4'-bis[(4-anilino-6-morpholino-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulfonate.
- 35 **Portion C** comprises, or even is constituted by, at least one organic or semi-organic macromolecular compound independently selected from the group G₂ or the group G₃

and with a molar mass in the range 5×10^2 g/mol to 10^5 g/mol.

Group G_2 is constituted by biocompatible compounds; biodegradable compounds; lipids; polysaccharides; proteins; glycoproteins; glycolipids; neutral or charged lipids selected from group H_1 constituted by fatty alcohols containing at least 10 carbon atoms in a linear or branched chain such as polyethyleneglycol (PEG), fatty acids containing at least 10 carbon atoms in a linear or branched chain; lecithin; sphingolipids; fatty amines containing at least 10 carbon atoms in a linear or branched chain; polyesters; polyamides; polyethers such as polyoxyethylene-9-lauryl-1-ether; polythioethers; polyureas; polycarbonates; polycarbamides; polyaryls; polysilicones selected from the group constituted by polydimethylsiloxanes (PDMS), phenylated polyorganosiloxanes such as phenyltrimethicones, phenyltrimethylsiloxydiphenylsiloxanes, diphenylmethyldimethyltrisiloxanes, diphenyldimethicones, phenyldimethicones or polymethylphenylsiloxanes, which may be fluorinated; polysiloxanes modified with fatty acids, with fatty alcohols or with polyoxyalkylenes, fluorosilicones and perfluorinated silicone oils, and mixtures thereof; volatile silicone oils such as cyclic or linear silicones, preferably with a viscosity at ambient temperature and at an atmospheric pressure of less than $8 \text{ mm}^2/\text{s}$ (8 cSt), and in particular containing 2 to 7 silicon atoms, (preferably octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, hexadecamethylcyclohexasiloxane, heptamethylhexyltrisiloxane or heptamethyloctyltrisiloxane).

Group G_3 is constituted by metallic oxides with a valency in the range 1 to 6, the metallic portion being constituted by metallic elements selected from the group H_2 constituted by the metals titanium, iron, copper, zinc, zirconium, strontium, indium, silicon, tin, tellurium, niobium, bismuth, cerium, yttrium, or their alloys, such

as TiO_2 , Fe_2O_3 , CuO , ZnO , Y_2O_3 , ZrO_2 , In_2O_3 , SiO_2 , SnO_2 , Ta_2O_5 , Bi_2O_3 , CeO_2 , SrO_2 , Si_xO_y x and y independently being in the range 0.1 to 2.

Portion C is preferably constituted by metallic
oxide, non-limiting examples being Si_xO_y , x and y
independently being in the range 0.1 to 2, titanium
oxides TiO_2 , silica SiO_2 , zirconium oxide ZrO_2 , iron
oxides Fe_2O_3 ; polysilicones such as polydimethylsiloxanes
(PDMS), phenylated polyorganosiloxanes;
polyethyleneglycol (PEG), poly(vinyl)pyrrolidinone PVP;
polyacrylates such as PMMA, for example; polystyrenes PS,
or polyureas.

Preferably, C is constituted by PMMA, PVP, PS, of
metallic oxide selected from Si_xO_y x and y independently
being in the range 0.1 to 2, titanium oxides TiO_2 , silicas
 SiO_2 .

Preferably, C is constituted by metallic oxide
selected from silicon oxides Si_xO_y , silicas SiO_2 , and
preferably silicas SiO_2 .

The thickness of the shells C of structure (I) or
(II) is preferably in the range 2 nm to 80 nm, preferably
in the range 10 nm to 50 nm, preferably in the range
20 nm to 30 nm.

Portion D comprises, or even is constituted by, at
least one organic or semi-organic polymeric compound
independently selected from groups G_2 and G_3 ; they may be
spherical in shape with a diameter in the range 20 nm to
250 nm, or cylindrical with the minor axis from 5 nm to
50 nm and the major axis from 20 nm to 250 nm (cf.
N. Halas, ACS Nano, 2009, 3(3), 744 to 752).

Portion D is preferably constituted by metallic
oxide, non-limiting examples being silicon oxides, Si_xO_y ,
x and y independently being in the range 0.1 to 2,
silicas SiO_2 , iron oxides Fe_2O_3 ; polyacrylates such as
PMMA, for example; polystyrenes PS, or polyureas.

Preferably, portion D is constituted by PMMA, PS, metallic oxides selected from Si_xO_y x and y independently being in the range 0.1 to 2, silicas SiO_2 .

Preferably, portion D is constituted by metallic
5 oxides selected from silicon oxides Si_xO_y , silicas SiO_2 ; and more preferably silicas SiO_2 .

Preferably, portion D has a core diameter ranging from 150 to 250 nm.

Portion E comprises, or even is constituted by a
10 metal selected from group G_1 .

Portion E is more preferably selected from the group constituted by the metals silver, or gold; more preferably gold.

Preferably, portion E has a thickness ranging from 5 to
15 30 nm.

Production methods

One example of a method of producing a particulate
20 material with structure (I) above may comprise steps consisting of initially mixing a precursor for portion C with a dispersion of portion A to obtain hybrid A+C particles, and secondly in dispersing said A+C particles in a solution or suspension containing at least one
25 fluorophore compound for portion B, then in a third stage in possibly isolating the final material.

One example of a method of producing a particulate material with structure (II) above may comprise steps consisting of initially mixing a precursor for portion E
30 with a dispersion of portion D to obtain hybrid D+E particles after isolation, and secondly in dispersing said D+E particles in a solution or suspension containing at least one precursor for portion C to obtain D+E+C particles after isolation, then in a third stage of
35 dispersing said D+E+C particles in a solution or suspension containing at least one luminescent compound

for portion B, then in a fourth stage in possibly isolating the final material.

In general, the fluorophore compound or compounds of the invention may be selected from the above list a) to 5 1), independently of whether structures (I) or (II) above are concerned.

GALENICAL DOSAGE FORMS

A composition of the invention may be solid or 10 fluid.

In the context of the invention, the term "solid" is used to mean a composition of high consistency, which retains its shape during storage. As opposed to compositions termed "fluid", it does not flow under its 15 own weight.

In first exemplary embodiments, a composition of the invention is in the solid form, and more particularly in the form of a pressed powder or a cast composition.

The term "pressed powder" means a mass of 20 composition of cohesion that is at least partially due to compacting during manufacture.

The term "cast composition" means a mass of composition of cohesion that is due to solidification of at least one of its constituents during production. The 25 composition may be hot cast into a mold, and solidification results from cooling it.

A cast composition of the invention may be in the anhydrous form or in the form of a solid emulsion. A solid emulsion does not flow under its own weight at 30 ambient temperature, in contrast to a conventional emulsion, and is in particular characterized by the presence of wax(es) in the liquid fatty phase.

In a variation, a composition of the invention may be in the fluid (liquid) form, with greater or lesser 35 viscosity, with a creamy or pasty appearance, such as in the form of an oily or aqueous solution, containing an

oily gel, or an oil-in-water, water-in-oil or multiple emulsion.

A composition of the invention must be cosmetically or dermatologically acceptable, namely contain a non-
5 toxic medium that is capable of being applied to the keratinous materials of human beings, in particular to the skin.

The term "cosmetically acceptable" as used in the context of the invention means a composition with an
10 agreeable appearance, odor and feel.

The medium is generally adapted to how the composition is to be packaged. In particular, the nature and the quantity of the various compounds are adapted, for example depending on whether the composition is
15 formulated into the solid or fluid form.

The composition of the invention may be in the form of a composition for makeup and/or care of keratinous materials, for example a blusher, an eye shadow, a face powder, a foundation, especially for application to the
20 face or neck, a concealer, a complexion corrector, a tinted cream, a lipstick, a lip balm, or a colored skin care or makeup composition, in particular for the face or body.

The skilled person will select the galenical dosage form that is suitable, in particular from fluid or solid forms that are suitable for topical application to keratinous materials, in particular the skin.
25

In particular, a composition of the invention may be in the form of a fluid, for example pasty or liquid, a
30 gel, a cream, or in the form of a free or pressed powder, or a cast composition. As an example, it may be an oil-in-water, water-in-oil or multiple emission, a solid emulsion in particular of the water-in-oil type, an aqueous or oily gel, a pressed or loose powder or a cast
35 composition, especially in the anhydrous form or in the form of a solid emulsion.

The composition may be packaged into a packaging and application device comprising an applicator, the application surface being defined, for example, by a brush, a sponge, a foam, a flocked membrane, a cloth or a nonwoven.

The composition may be applied by spraying or transfer, if appropriate.

Aqueous phase

A composition of the invention may comprise an aqueous phase.

An aqueous phase comprises water. Water suitable for use in the invention may be a floral water such as cornflower water and/or mineral water such as VITTEL water, LUCAS water or ROCHE POSAY water and/or a thermal water.

The aqueous phase may also comprise organic solvents that are miscible with water (at ambient temperature, 25°C) such as, for example, mono-alcohols containing 2 to 6 carbon atoms such as ethanol, isopropanol; polyols in particular containing 2 to 20 carbon atoms, preferably containing 2 to 10 carbon atoms, and more preferably containing 2 to 6 carbon atoms, such as glycerol, propylene glycol, butylene glycol, pentylene glycol, hexylene glycol, dipropylene glycol, diethylene glycol; glycol ethers (in particular containing 3 to 16 carbon atoms) such as mono, di- or tripropylene glycol(C₁-C₄)alkylethers, mono, di- or triethylene glycol(C₁-C₄) alkyl ethers, and mixtures thereof.

The aqueous phase may further comprise stabilizing agents, for example sodium chloride, magnesium dichloride, and magnesium sulfate.

The aqueous phase may also comprise any hydrosoluble or hydrodispersible compound that is compatible with an aqueous phase such as gelling agents, film-forming polymers, thickeners, surfactants, and mixtures thereof.

In particular, a composition of invention may comprise an aqueous phase in an amount in the range 1% to 80% by weight, in particular in the range 5% to 50%, and more particularly in the range 10% to 45% by weight relative to the total composition weight.

In other exemplary embodiments, a composition of invention may be anhydrous.

An anhydrous composition may comprise less than 3% by weight of water, relative to the total composition weight, and in particular less than 2%, especially less than 1% by weight water relative to the total composition weight, water not being added during preparation of the composition but corresponding to the residual water supplied by the mixed ingredients.

More particularly, an anhydrous composition may be completely free of water.

Fatty phase

A cosmetic composition of the invention may comprise at least one liquid and/or solid fatty phase.

In particular, a composition of the invention may comprise at least one liquid fatty phase, especially comprising at least one oil as mentioned below.

The term "oil" means any fat in the liquid form at ambient temperature (20°C to 25°C) and at atmospheric pressure.

A composition of the invention may comprise a liquid fatty phase in a quantity in the range 1% to 90% by weight, in particular in the range 5% to 80%, in particular in the range 10% to 70% by weight, and more particularly in the range 20% to 50% by weight relative to the total composition weight.

The oily phase suitable for the preparation of cosmetic compositions in accordance with the invention may comprise hydrocarbon oils, silicone oils fluorinated or otherwise, or mixtures thereof.

The oils may be volatile or non-volatile.

They may be of animal, vegetable, mineral or synthetic origin.

In the context of the present invention, the term "volatile oil" means an oil (or non-aqueous medium) susceptible of evaporating in contact with the skin in at least one hour, at ambient temperature and at atmospheric pressure. The volatile oil is a cosmetic volatile oil that is liquid at ambient temperature, in particular having a non-zero vapor pressure at ambient temperature and at atmospheric pressure, in particular, having a vapor pressure in the range 0.13 Pa to 40000 Pa (10^{-3} mm to 300 mm Hg), preferably in the range 1.3 Pa to 13000 Pa (0.01 mm to 100 mm Hg), and more preferably in the range 1.3 Pa to 1300 Pa (0.01 mm to 10 mm Hg).

In the context of the present invention, the term "non-volatile oil" means an oil having a vapor pressure of less than 0.13 Pa.

In the context of the present invention, the term "silicone oil" means an oil comprising at least one silicon atom, and in particular at least one Si-O group.

The term "fluorinated oil" means an oil comprising at least one fluorine atom.

The term "hydrocarbon oil" means an oil principally containing hydrogen and carbon atoms.

The oils may optionally comprise atoms of oxygen, nitrogen, sulfur and/or phosphorus, for example in the form of hydroxyl or acid radicals.

Volatile oils

The volatile oils may be selected from hydrocarbon oils containing 8 to 16 carbon atoms, and in particular C_8 - C_{16} branched alkanes (also termed isoparaffins), such as isododecane (also termed 2,2,4,4,6-pentamethylheptane), isodecane, isohexadecane and, for example, oils sold under the commercial names ISOPARS® or PERMETHYLS®.

It is also possible to use volatile silicones as the volatile oils such as, for example, linear or cyclic volatile silicone oils, in particular those with a viscosity ≤ 8 centistokes ($8 \times 10^{-6} \text{ m}^2/\text{s}$), and in particular containing 2 to 10 silicon atoms, especially 2 to 7 silicon atoms, these silicones optionally comprising alkyl or alkoxy groups containing 1 to 10 carbon atoms. Examples of volatile silicone oils that may be used in the invention that may be mentioned are dimethicones with a viscosity of 5 and 6 cSt, octamethyl cyclotetrasiloxane, decamethyl cyclopentasiloxane, dodecamethyl cyclohexasiloxane, heptamethyl hexyltrisiloxane, heptamethyloctyl trisiloxane, hexamethyl disiloxane, octamethyl trisiloxane, decamethyl tetrasiloxane, dodecamethyl pentasiloxane and mixtures thereof.

It is also possible to use fluorinated volatile solvents such as nonafluoromethoxybutane or perfluoromethylcyclopentane, and mixtures thereof.

In one embodiment, the composition of the invention may comprise 1% to 80% by weight, or even 5% to 70% by weight, or even 10% to 60% by weight and in particular 15% to 50% by weight of volatile oil relative to the total composition weight.

Non-volatile oils

The non-volatile oils may, in particular, be selected from non-volatile hydrocarbon oils, fluorinated oils and/or silicone oils.

Non-volatile hydrocarbon oils that may in particular be mentioned are:

- hydrocarbon oils of animal origin such as perhydnosqualene;
- hydrocarbon oils of vegetable origin such as phytostearyl esters, for example phytostearyl oleate, phytostearyl isostearate and lauroyl/octyldodecyl/phytostearyl glutamate (AJINOMOTO,

ELDEW PS203), triglycerides constituted by esters of fatty acids and glycerol, in particular in which the fatty acids may have chain lengths from C_4 to C_{36} , in particular, C_{18} to C_{36} , said oils possibly being linear or
5 branched, saturated or unsaturated; said oils may in particular be heptanoic or octanoic triglycerides, shea, luzerne, poppy, Hokkaido squash, millet, barley, quinoa, rye, bancoulier, or passiflora oil, shea butter, aloe oil, sweet almond oil, peach kernel oil, peanut oil,
10 argan oil, avocado oil, baobab oil, borage oil, broccoli oil, calendula oil, cameline seed oil, canola oil, carrot oil, carthame oil, hemp oil, rapeseed oil, cottonseed oil, coprah oil, pumpkin seed oil, wheatgerm oil, jojoba oil, lys oil, macadamia oil, corn oil, meadowfoam oil,
15 hypericum oil, monoi oil, hazelnut oil, apricot kernel oil, walnut oil, olive oil, evening primrose oil, palm oil, blackcurrant seed oil, kiwi seed oil, grapeseed oil, pistachio oil, Hokkaido squash oil, pumpkin oil, quinoa oil, musk rose oil, sesame oil, soy oil, sunflower seed
20 oil, castor oil, and watermelon oil, and mixtures thereof, or triglycerides of caprylic/capric acids, such as those sold by the supplier STEARINERIES DUBOIS or those sold under the names MIGLYOL 810[®], 812[®] and 818[®] by the supplier DYNAMIT NOBEL;
25 • linear or branched hydrocarbons of mineral or synthetic origin, such as paraffin oils and derivatives thereof, Vaseline, polydecenes, polybutenes, or hydrogenated polyisobutene such as Parleam, squalane;
 • synthesized ethers containing 10 to 40 carbon
30 atoms;
 • synthesized esters such as oils with formula R_1COOR_2 , in which R_1 represents a residue of a linear or branched fatty acid containing 1 to 40 carbon atoms, and R_2 represents a hydrocarbon chain, in particular branched
35 containing 1 to 40 carbon atoms provided that $R_1 + R_2$ is ≥ 10 . The esters may in particular be selected from esters of an alcohol and a fatty acid, such as, for

- example: cetostearyl octanoate, esters of isopropyl alcohol such as isopropyl myristate, isopropyl palmitate, ethyl palmitate, 2-ethyl-hexyl palmitate, isopropyl stearate or isostearate, isostearyl isostearate, octyl
- 5 stearate, hydroxylated esters such as isostearyl lactate, octyl hydroxystearate, diisopropyl adipate, heptanoates, in particular isostearyl heptanoate, octanoates, decanoates or ricinoleates of alcohols or polyalcohols, such as propylene glycol dioctanoate, cetyl octanoate,
- 10 tridecyl octanoate, ethyl 2-hexyl 4-diheptanoate and palmitate, alkyl benzoate, polyethylene glycol diheptanoate, propylene glycol 2-diethyl hexanoate, and mixtures thereof, C₁₂-C₁₅ alcohol benzoates, hexyl laurate, esters of neopentanoic acid, such as isodecyl
- 15 neopentanoate, isotridecyl neopentanoate, isostearyl neopentanoate, octyldodecyl neopentanoate, esters of isononanoic acid such as isononyl isononanoate, isotridecyl isononanoate, octyl isononanoate, and hydroxyl esters such as isostearyl lactate or di-
- 20 isostearyl malate;
- esters of polyols and esters of pentaerythritol, such as dipentaerythritol tetrahydroxystearate/tetraisostearate;
 - esters of dimeric diols and dimeric diacids, such
- 25 as Lusplan DD-DA5® and Lusplan DD-DA7®, sold by the supplier nippon fine chemical and described in application US 2004-175338;
- copolymers of dimeric diols and dimeric diacids and esters thereof, such as copolymers of dilinoleyl diol
- 30 dimers / dilinoleic dimers and esters thereof, such as, for example Plandool-G;
- copolymers of polyols and dimeric diacids and esters thereof, such as Hailuscent ISDA, or dilinoleic acid/butanediol copolymer;
- 35 • fatty alcohols that are liquid at ambient temperature with a branched and/or unsaturated chain containing 12 to 26 carbon atoms, such as 2-

octyldodecanol, isostearyl alcohol, oleic alcohol, 2-hexyldecanol, 2-butyloctanol or 2-undecylpentadecanol;

• higher C_{12} - C_{22} fatty acids such as oleic acid, linoleic acid, linolenic acid, and mixtures thereof; and
5 di-alkyl carbonates, the 2 alkyl chains possibly being identical or different, such as dicaprylyl carbonate sold in particular under the name CETIOL CC[®] by COGNIS;

• oils with a high molar mass, in particular a molar mass from approximately 400 to approximately 10000 g/mol, in particular from approximately 650 to approximately 10000 g/mol, in particular from approximately 750 to approximately 7500 g/mol, and more particularly from approximately 1000 to approximately 5000 g/mol. High molar mass oils that may be used in the present invention
15 that may in particular be mentioned are oils selected from:

- lipophilic polymers;
- esters of linear fatty acids with a total number of carbon atoms in the range 35 to 70;
- 20 • hydroxylated esters;
- aromatic esters;
- esters of branched C_{24} - C_{28} fatty acids or fatty alcohols;
- silicone oils;
- 25 • oils of vegetable origin;
- and mixtures thereof;
- fluorinated oils, optionally partially hydrocarbonaceous and/or siliconaceous, such as fluorosilicone oils, fluorinated polyethers or
30 fluorinated silicones such as those described in the document EP-A-0 847 752; and
- silicone oils such as non-volatile, linear or cyclic polydimethylsiloxanes (PDMS), polydimethylsiloxanes comprising alkyl, alkoxy or phenyl
35 groups that may be pendent or at the end of the silicon chain, groups containing 2 to 24 carbon atoms; phenyl silicones such as phenyl trimethicones, phenyl

dimethicones, phenyl trimethylsiloxyl diphenylsiloxanes, diphenyl dimethicones, diphenyl methyl diphenyl trisiloxanes, or 2-phenylethyl trimethylsiloxysilicates; and mixtures thereof.

5

Pasty compounds

A composition in accordance with the invention may further comprise at least one pasty compound.

10 The presence of a pasty compound can advantageously provide improved comfort during deposition of a composition of the invention.

Said compound may advantageously be selected from lanolin and derivatives thereof; polymeric or non-polymeric silicone compounds; polymeric or non-polymeric
15 fluorinated compounds; vinyl polymers, in particular olefin homopolymers; olefin copolymers; homopolymers and copolymers of hydrogenated dienes; linear or branched oligomers, homo or copolymers of alkyl (meth)acrylates preferably containing a C₈-C₃₀ alkyl group; homo- and
20 copolymeric oligomers of vinyl esters containing C₈-C₃₀ alkyl groups; homo- and copolymeric oligomers of vinyl ethers containing C₈-C₃₀ alkyl groups; liposoluble polyethers resulting from polyetherification between one or more C₂-C₁₀₀ diols, in particular C₂-C₅₀; fatty acid or
25 alcohol esters; and mixtures thereof.

The following esters may in particular be mentioned: esters of a glycerol oligomer, in particular diglycerol esters, such as polyglyceryl-2 triisostearate, condensates of adipic acid and glycerol, wherein a
30 portion of the hydroxyl groups of the glycerols has been reacted with a mixture of fatty acids such as stearic acid, capric acid, stearic and isostearic acid and 12-hydroxystearic acid, especially similar to those sold with reference Softisan 649 by the supplier Sasol or such
35 as bis-diglyceryl polyacyladipate-2; arachidyl propionate sold in particular with reference Waxenol 801 by the supplier Alzo; phytosterol esters; triglycerides of fatty

acids and derivatives thereof, such as hydrogenated cocoglycerides; uncured polyesters resulting from polycondensation between a dicarboxylic acid or a linear or branched C₄-C₅₀ carboxylic polyacid and a C₂-C₅₀ diol or a polyol; aliphatic esters of esters resulting from the esterification of an ester of an aliphatic hydroxycarboxylic acid by an aliphatic carboxylic acid; polyesters resulting from esterification, by a polycarboxylic acid, of an aliphatic hydroxycarboxylic acid ester, said ester comprising at least two hydroxyl groups, such as the products Risocast DA-H[®], and Risocast DA-L[®]; and mixtures thereof.

The pasty compound or compounds may be present in the composition of the invention in a quantity in the range 0.1% to 30% by weight, preferably in the range 0.5% to 20% by weight, relative to the total composition weight.

A composition of the invention may comprise at least one powdered phase, said powdered phase in particular comprising at least one filler, and advantageously also at least one emissive material as defined above and/or at least one pigment.

This is particularly true of compositions in the form of powders, in particular pressed powders.

25

Fillers

The term "fillers" means particles of any shape, colorless or white, mineral or synthesized, insoluble in the medium for the composition irrespective of the temperature at which the composition is manufactured.

The fillers may be mineral or organic, of any shape, be they flake, spherical or oblong, irrespective of its crystallographic form (for example flake, cubic, hexagonal, orthorhombic, etc.). Mention may be made of talc, mica, silica, kaolin, polyamide powders (Nylon[®]) poly-β-alanine and polyethylene, tetrafluoroethylene polymer powders (Teflon[®]), lauroyl-lysine, starch, boron

nitride, bismuth oxychloride, hollow polymeric microspheres such as those formed from polyvinylidene chloride /acrylonitrile, such as Expancel[®] (Nobel Industrie), acrylic acid copolymers, silicone resin
5 microbeads (Tospearls[®] from the supplier Toshiba, for example), particles of polyorganosiloxane elastomers, precipitated calcium carbonate, magnesium carbonate and bicarbonate, hydroxyapatite, barium sulfate, aluminum oxides, polyurethane powders, composite fillers, hollow
10 silica microspheres, glass or ceramic microcapsules, metallic salts derived from organic carboxylic acids containing 8 to 22 carbon atoms, preferably 12 to 18 carbon atoms, for example zinc, magnesium or lithium stearate, zinc laurate, or magnesium myristate.

15 In preferred exemplary embodiments, at least one filler is used selected from kaolin, polyamide powders (Nylon), copolymers of acrylic acid, and mixtures thereof.

The filler or fillers may be present in a
20 composition according to the invention in a total quantity of fillers in the range 0.1% to 96% by weight relative to the total weight of the composition, preferably in the range 1% to 85% by weight, and more preferably in the range 5% to 80% by weight.

25 With a fluid composition, for example, the filler or fillers may generally be present in a quantity in the range 0.1% to 20% by weight, preferably in the range 0.5% to 15% by weight relative to the total composition weight, in particular 1% to 7% by weight relative to the
30 total composition weight.

With a solid composition in the form of a powder, the filler or fillers may generally be present in a quantity in the range 50% to 96% by weight, in particular in the range 70% to 85% by weight, preferably in the
35 range 75% to 80% by weight relative to the total composition weight.

Pigments and colorizing agents

In addition to the emissive materials of the invention, the composition of the invention may comprise one or more pigments or colorizing agents.

5 The term "pigments" should be understood to mean particles in any form, white or colored, mineral or organic, insoluble in the physiological medium, intended to color the composition.

10 The pigments may be white or colored, mineral and/or organic. Mineral pigments that may be mentioned include titanium dioxide, optionally surface treated, oxides of zirconium or cerium, as well as oxides of zinc, iron (black, yellow or red) or of chromium, manganese violet, ultramarine blue, chromium hydrate and ferric blue,
15 powdered metals such as aluminum powder, and copper powder.

 Organic pigments that may be used that may be mentioned are carbon black, D & C type pigments and lakes, especially lakes based on carmine and cochineal,
20 barium, strontium, calcium and aluminum.

 Opaque pigments, such as iron oxides, for example, may be present in the composition of the invention in a quantity in the range 0.1% to 15% by weight relative to the total composition weight, preferably in the range
25 0.5% to 10% by weight, and preferably in the range 1% to 10% by weight.

 The composition of the invention may comprise an additional powdered colorizing material that is different from the pigments described above, and may in particular
30 be selected from nacles and other interference pigments, flakes and mixtures thereof.

 The nacles may be selected from white nacles such as mica coated with titanium or bismuth oxychloride, colored nacles such as mica titanium coated with oxides of iron,
35 in particular mica titanium coated with ferric blue or chromium oxide, mica titanium coated with an organic

pigment of the above-mentioned type and nacres based on bismuth oxychloride.

The nacres may be present in a composition in accordance with the invention in a quantity in the range
5 0.1% to 50% by weight relative to the total composition weight, preferably in the range 0.1% to 40% by weight, and more preferably in the range 0.1% to 30% by weight.

The colorizing agents may be selected from those listed in Annex 4 of the European Cosmetics Directive and
10 those listed by the FDA as authorized for cosmetics.

Additives for powder phase

A composition according to the invention may comprise at least one agent for structuring the liquid
15 fatty phase selected from a wax, a silicone resin and mixtures thereof.

Waxes

The term "wax" as used in the context of the present
20 invention means a lipophilic fatty compound that is solid at ambient temperature (25°C) and atmospheric pressure (760 mm Hg, i.e. 10^5 Pa), with a reversible solid/liquid change of state, in particular having a melting temperature greater than or equal to 30°C, in particular
25 greater than or equal to 55°C, and possibly up to 250°C, especially up to 230°C, and in particular up to 120°C.

By heating the wax to its temperature of melting, it is possible to render it miscible with the oils and to form a microscopically homogeneous mixture, but on re-
30 establishing the temperature of the mixture at ambient temperature, the wax re-crystallizes in the oils of the mixture.

The waxes may be present in the composition in accordance with the invention in a quantity in the range
35 0.1% to 15% by weight relative to the pulverulent phase, preferably in the range 1% to 8%.

The values for the melting point in accordance with the invention correspond to the melting peak measured using a differential scanning calorimeter (DSC), for example the calorimeter sold under the name DSC 30 by the supplier METLER, with a temperature rise rate of 5°C or 10°C per minute.

In the context of the invention, the waxes may be those generally used in the cosmetic or dermatological fields. In particular, they may be hydrocarbons, silicone and/or fluorinated, optionally comprising ester or hydroxyl functions. They may also be of natural or synthetic origin.

Illustrative, non-limiting examples of said waxes that may in particular be mentioned are:

- waxes of animal origin such as beeswax, vegetable waxes such as carnauba, candellila, ouricury, Japan wax;
- mineral waxes, for example paraffin wax, or microcrystalline waxes or ozokerites,
- synthetic waxes including polyethylene waxes, and the waxes obtained by Fisher-Tropsch synthesis;
- silicone waxes, in particular substituted linear polysiloxanes; mention may be made, for example, of silicone polyether waxes, alkyl or alkoxy-dimethicones containing 16 to 45 carbon atoms, and alkyl methicones such as C₃₀-C₄₅ alkyl methicone sold under the trade name "AMS C 30" from the supplier DOW CORNING,
- hydrogenated oils that are solid at 25°C such as hydrogenated castor oil, hydrogenated jojoba oil, hydrogenated palm oil, hydrogenated tallow, hydrogenated coconut oil and fatty esters that are solid at 25°C such as C₂₀-C₄₀ alkyl stearate sold under the trade name "KESTER WAX K82H" by the supplier KOSTER KEUNEN,
- and/or mixtures thereof.

In accordance with exemplary embodiments, the wax present in the composition of the invention may be completely or partially in the powder form, in particular micronized, to facilitate its use in the preparation of

the cosmetic composition, especially when it is in the form of a powder.

Examples of waxes that may be used in the powder form that may be mentioned are carnauba wax microbeads sold under the name Microcare 350[®] by the supplier Micro Powders and paraffin wax microbeads sold under the name Microease 114S[®] by the supplier Micro Powders. Such additional micronized waxes may in particular improve the properties during application of the composition to the skin.

Silicone resins

The pulverulent phase of a composition of the invention may further comprise at least one silicone resin.

Silicone resins are the products of hydrolysis and polycondensation of mixtures of siloxanes with formulas $(R)_3SiOCH_3$ and $Si(OCH_3)_4$, R representing an alkyl group containing 1 to 6 carbon atoms.

Said silicone resins are known or can be prepared using known methods. Examples of commercially available silicone resins that may be mentioned are those sold under the names KSP 100 (SHIN ETSU).

The silicone resin may be present in a quantity in the range 0.1% to 35% by weight relative to the total weight of the pulverulent phase.

Other ingredients

A composition in accordance with the invention may comprise any other ingredients (adjuvant) that is in routine use in cosmetics such as thickening or gelling agents, film-forming polymers, vitamins, oligo-elements, softeners, sequestering agents, fragrances, alkalizing or acidifying agents, preservatives, sunscreens, surfactants, anti-oxidants, cosmetic active ingredients, moisturizers, or mixtures thereof.

Clearly, the skilled person will take care to select any complementary compounds and/or their quantity such that the advantageous properties intrinsically attached to the composition of the invention are not or are not substantially altered by the envisaged addition.

The invention is illustrated in the examples given below by way of non-limiting illustration.

Unless otherwise indicated, the values in the examples below are expressed as a % by weight of the total composition weight.

EXAMPLES

Examples 1 to 12 of particulate materials with structure (I)

Method for obtaining said materials

1st step: Preparation of A-C in accordance with Figure 4

Synthesis of Ag@SiO₂ and Au@SiO₂ nanospheres

The nanospheres were synthesized using the protocols described by G. Chumanov, Chem. Phys. Chem., 2005, 6, 1221 - 1231; J. Phys. Chem. B, 2004, 108, 1522 - 1524; Nano Lett. 2001, 1, 647 - 649; J. Am. Chem. Soc. 1999, 121, 10642 - 10643; H.C. Gerritssen, Adv. Matter., 2006, 18, 91 - 95; A. van Blaaderen, Langmuir, 2003, 19, 6693 - 6700; Langmuir, 2003, 19, 1384 - 1389.

The gold, spherically shaped nanospheres with a diameter of 5 nm, 50 nm, 80nm, 100 nm, 200 nm were supplied by the supplier Ted Pella Inc.

The silver, spherically shaped nanospheres with a diameter of 20 nm, 40 nm, 60 nm, 80 nm, 100nm, 110nm were supplied by the supplier Ted Pella Inc.

Protocol 1: Synthesis of Ag@SiO₂ and Au@SiO₂ nanospheres

An aqueous solution of poly(vinylpyrrolidone) PVP with a molar mass of 360 kg/mol and an aqueous suspension

of spherical noble metal (gold or silver) colloids with a diameter d (nm) were mixed at ambient temperature for 24h under vigorous agitation. The quantity of PVP was calculated such that the number of PVP molecules was approximately 60 per nm².

After centrifuging the colloids obtained, the liquid supernatant was withdrawn. The colloids were then dispersed in an ethanolic solution of ammonia (4.2%v/v) and an ethanolic solution of tetraethoxysilane (TEOS), 10%v/v, was introduced at ambient temperature with vigorous agitation. The TEOS hydrolysis reaction was of a duration of 12 h at ambient temperature then the dispersed colloids obtained were centrifuged and washed with water three times then re-dispersed in 20 mL of water. The relative concentration of TEOS allowed the thickness of the silica shell to be controlled.

The following silver and gold silica-enveloped colloids were thus obtained (r_1 and r_2 are shown in Figure 1A):

20

$[Ag@SiO_2]_{40,60}$: $r_1 = 40 \pm 5$ nm; $r_2 = 60 \pm 3$ nm
 $[Ag@SiO_2]_{40,70}$: $r_1 = 40 \pm 5$ nm; $r_2 = 70 \pm 3$ nm
 $[Ag@SiO_2]_{60,80}$: $r_1 = 60 \pm 5$ nm; $r_2 = 80 \pm 3$ nm
 $[Ag@SiO_2]_{60,90}$: $r_1 = 60 \pm 5$ nm; $r_2 = 90 \pm 3$ nm
 $[Ag@SiO_2]_{80,100}$: $r_1 = 80 \pm 5$ nm; $r_2 = 100 \pm 3$ nm
 $[Ag@SiO_2]_{80,110}$: $r_1 = 80 \pm 5$ nm; $r_2 = 100 \pm 3$ nm
 $[Ag@SiO_2]_{110,130}$: $r_1 = 110 \pm 5$ nm; $r_2 = 130 \pm 3$ nm
 $[Ag@SiO_2]_{110,140}$: $r_1 = 110 \pm 5$ nm; $r_2 = 140 \pm 3$ nm

 $[Au@SiO_2]_{50,70}$: $r_1 = 50 \pm 3$ nm; $r_2 = 70 \pm 2$ nm
 $[Au@SiO_2]_{50,75}$: $r_1 = 50 \pm 3$ nm; $r_2 = 75 \pm 2$ nm
 $[Au@SiO_2]_{80,100}$: $r_1 = 80 \pm 3$ nm; $r_2 = 100 \pm 2$ nm
 $[Au@SiO_2]_{80,110}$: $r_1 = 80 \pm 3$ nm; $r_2 = 110 \pm 2$ nm
 $[Au@SiO_2]_{100,120}$: $r_1 = 100 \pm 3$ nm; $r_2 = 120 \pm 2$ nm
 $[Au@SiO_2]_{100,130}$: $r_1 = 100 \pm 3$ nm; $r_2 = 130 \pm 2$ nm

Protocol 2: Synthesis of Ag@SiO₂ nanospheres

An iso-propanolic solution was mixed with deionized water and an aqueous colloidal suspension of silver. A solution of ammonium hydroxide, 30%v/v at ambient temperature, then tetraethoxysilane (TEOS) was added to this suspension under vigorous agitation. After 15 minutes agitation at ambient temperature, the suspension was allowed to stand for 24h at 4°C before being centrifuged and washed with water three times then re-dispersed in 20 mL of water. The relative concentration of TEOS allowed the thickness of the silica shell to be controlled.

The following silica-enveloped silver colloids were thus obtained (r_1 and r_2 refer to Figure 1A):

[Ag@SiO₂]_{85,95}: $r_1 = 85 \pm 5$ nm; $r_2 = 95 \pm 3$ nm
[Ag@SiO₂]_{85,106}: $r_1 = 85 \pm 5$ nm; $r_2 = 106 \pm 3$ nm
[Ag@SiO₂]_{85,125}: $r_1 = 85 \pm 5$ nm; $r_2 = 125 \pm 3$ nm

Protocol 3: Synthesis of Ag@PMMA and Au@PMMA nanospheres

The protocol described in J Am Chem Soc 1999, 121, 10642 - 10643 was followed.

Protocol 4: Synthesis of Ag@PVP and Au@PVP nanospheres

The protocol described in Nano Lett. 2001, 1, 647 - 649 was followed.

2nd step: Method for obtaining composite emissive materials

Materials doped with fluorophores were produced using the protocols described in the following publications:

· W.L. Vos, J. Phys. Chem. B. 1999, 103 (9), pp 1408 - 1415; I. Sokolov, Smal 2007, 3, 3, 419 - 4123; Small 2008, 4, 7, 934 - 939; N. Halas, Small 2008, 4, 10, 1716 - 1722; A.E. Ostafin, J. Non-Crystal Sol. 2007, 353, 354 - 365; W.H. Tan, Adv Mater 2004, 16, 173 - 176; Anal. Bioannal. Chem. 2006, 385, 518 - 524; Nano Lett. 2006, 6, 1, 84 - 88; Langmuir 2004, 20, 8336 - 8342; Langmuir

2001, 17, 4812 - 4817; J. Nanosci. NanoTechnol. 2002, 2, 405 - 409; J.Z. Zhou, Anal. Chem. 2004, 76, 5302 - 5312; D. Levy, Langmuir 2000, 16, 7377 - 7382.

5 General protocol 7a:

(3-aminopropyl)triethoxysilane APTES was added under vigorous agitation to a suspension of Ag@SiO₂ or Au@SiO₂ nanospheres, in deionized water at ambient temperature. After 30 min of reaction, the suspension of thus
10 functionalized colloids was centrifuged and washed three times with deionized water, then taken up in suspension in deionized water. 5 equivalents of fluorophore dissolved in ethanol was then added dropwise to this aqueous suspension and at ambient temperature and
15 agitated for 30 minutes. After leaving to stand for 24 h and at a temperature of 4°C, the suspension was centrifuged and washed several times with a deionized water/ethanol mixture until the washing water was free of residual fluorophore.

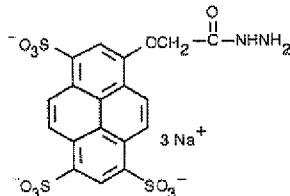
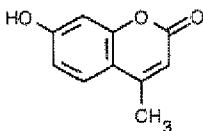
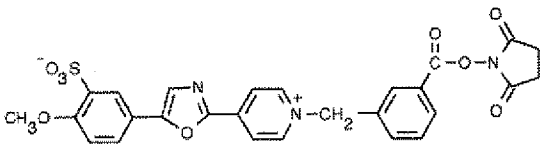
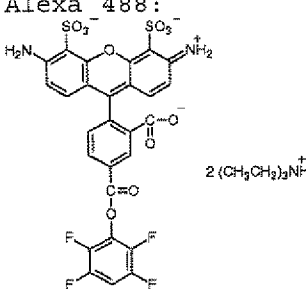
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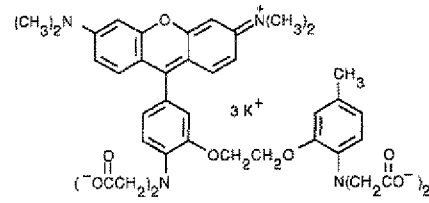
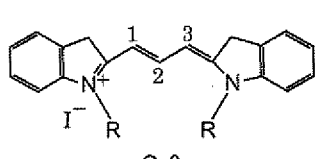
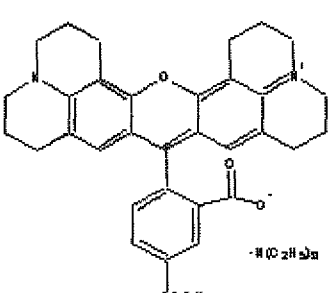
General protocol 7b:

A phenyltriethoxysilane (PTES)/tetraethoxysilane (TEOS) mixture was added under vigorous agitation to a suspension of Ag@SiO₂ or Au@SiO₂ nanospheres in deionized
25 water at ambient temperature. After 30 minutes of reaction, the suspension of colloids was centrifuged and washed three times with deionized water, then taken up into suspension in deionized water. 5 equivalents of fluorophore dissolved in ethanol was then added dropwise
30 to this aqueous suspension and at ambient temperature and agitated for 30 minutes. After leaving to stand for 24 h and at a temperature of 4°C, the suspension was centrifuged and washed several times with a deionized water/ethanol mixture until the washing water was free of
35 residual fluorophore.

General protocol 7c:

- 5 equivalents of a fluorophore dissolved in ethanol was added dropwise to a suspension of Ag@SiO₂ or Au@SiO₂ nanospheres in deionized water and at ambient temperature and agitation was carried out for 30 minutes. After leaving to stand for 24 h and at a temperature of 4°C, the suspension was centrifuged and washed several times with a deionized water/ethanol mixture until the washing water was free of residual fluorophore.
- The following fluorescent emissive composite materials were obtained:

Ex1: [Ag@SiO ₂ - Cascade Blue] _{40,60}	Cascade Blue: 
Ex2: [Ag@SiO ₂ - 7-hydroxy-4-methylcoumarin] _{40,60}	7-hydroxy-4-methylcoumarin: 
Ex3: [Ag@SiO ₂ - Cascade Yellow] _{80,100}	Cascade Yellow 
Ex4: [Ag@SiO ₂ - Alexa 488] _{80,100}	Alexa 488: 
Ex5: [Ag@SiO ₂ - Rhod-2] _{100,130}	Rhod-2:

Ex6: [Ag@SiO₂ - Cy3]_{100,130} Ex7: [Ag@SiO₂ - Fluoresceine]_{100,130} Ex8: [Ag@SiO₂ - 5-ROX]_{100,130} 5-ROX: 5-carboxy-X-Rhodamine Ex9: [Au@SiO₂ - cascade yellow]_{80,110} Ex10: [Au@SiO₂ - 5-ROX]_{80,110}	 Cy3:  Spiro(isobenzofuran-1(3H), 9'-(9H)xanthen)-3-one, 3',6'-dihydroxy-5-amino- 5-ROX:  Ex9: [Au@SiO₂ - cascade yellow]_{80,110}
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Examples 11 and 12: particulate materials with structure (II):

- 5 1st step: Preparation of C-D-E of Figure 5, namely a silica core coated with metal and a silica shell.

A triplet of values, for example 250, 270, 290, denotes a structure where r_1 , r_2 and r_3 are respectively 250 nm, 270 nm, and 290 nm.

- 10 The particles of type SiO₂ @ M @ SiO₂ (M represents Au or Ag) were manufactured using the protocols described in the following publications: N.J. Halas, Small 2008, 4 10, 1716 - 1722; W. Stöber, J. Colloid Interface Science, 26, 62 - 69, 1968; D.G. Duff described in Langmuir, 1993,
- 15 9, 2301.

Protocol 8: Production of $[\text{SiO}_2@\text{Au}@\text{SiO}_2]_{250,270,290}$ and $[\text{SiO}_2@\text{Au}@\text{SiO}_2]_{250,290,310}$ nanospheres

In a first step, the silica nanospheres with a
5 diameter in the range 50 nm to 300 nm were produced using
the protocol described by W. Stöber, J. Colloid Interface
Science, 26, 62 - 69, 1968 by hydrolyzing
tetraethoxysilane (TEOS) with a saturated basic ammonium
hydroxide solution in a lower alcohol such as ethanol or
10 a 3:1 mixture of propanol: methanol at ambient
temperature and under mechanical agitation.

70 mmole of TEOS was added to an ethanolic solution of
105 mmole of ammonium hydroxide with mechanical agitation
in a 500 mL flask. After introducing 25 mL of deionized
15 water, the reaction medium was left to stand for 24 h.
The reaction medium was then allowed to return to ambient
temperature and the ethanol and ammonia were evaporated
off under reduced pressure. After repeated washing with
ethanol, 1 g of powder corresponding to silica
20 nanospheres 250 ± 10 nm in diameter were isolated.

After adding 100 mL of ethanol to said nanospheres,
1.5 eq of (3-aminopropyl)trimethoxysilane (APTES) was
introduced with vigorous agitation and the reaction was
carried out for 24 h then was heated under reflux for
25 1 h. After cooling to ambient temperature, the reaction
medium was centrifuged and washed with ethanol three
times and the silica nanospheres functionalized with
amine terminal groups were recovered in suspension in
50 mL of ethanol.

30 40 mL of a normal solution of sodium chloride at ambient
temperature then 200 mL of a solution of 2 nm to 3 nm
diameter gold nanospheres prepared in accordance with the
method by D.G. Duff described in Langmuir, 1993, 9, 2301
were added, with agitation, to 10 mL of an ethanolic
35 suspension of functionalized silica nanospheres. After
agitating for 12 h, the colloidal solution of $\text{SiO}_2@\text{Au}$

nanospheres was centrifuged and washed with water three times, then redispersed in 100 mL of deionized water.

The dispersion of the thus embellished $\text{SiO}_2\text{@Au}$ nanospheres obtained (5 mL) was then mixed, with
5 agitation, and at ambient temperature with 300 mL of an aqueous 0.1% solution of gold tetrachloric acid HAuCl_4 containing 1.3 g of potassium carbonate. After 15 minutes, 1.5 mL of 38% formaldehyde in water was introduced and the reaction was agitated for 1 h 30.
10 After centrifuging and washing with water three times, $\text{SiO}_2\text{@Au}$ silica nanospheres enveloped with a continuous shell of gold with a thickness of 40 ± 5 nm were obtained and were redispersed in 10 mL of water.

By selecting a dispersion of 10 mL of $\text{SiO}_2\text{@Au}$
15 nanospheres thus embellished with gold, an aqueous suspension of $\text{SiO}_2\text{@Au}$ nanospheres enveloped with a continuous shell of gold with a thickness of 20 ± 5 nm was obtained.

The $\text{SiO}_2\text{@Au}$ nanospheres in aqueous dispersion were
20 introduced into pure ethanol at ambient temperature and with vigorous agitation. A 30% solution of ammonium hydroxide along with a tetraethylsiloxane (TEOS) solution were simultaneously added to this dispersion, with vigorous agitation for 1 h. The quantity of TEOS added
25 was adjusted so as to control the thickness of the silica shell obtained around the $\text{SiO}_2\text{@Au}$ nanospheres.

After leaving overnight at 4°C , the $\text{SiO}_2\text{@Au@SiO}_2$ nanospheres were centrifuged and washed several times with water then redispersed in 20 mL of water.

30 The following $\text{SiO}_2\text{@Au@SiO}_2$ silica colloids were thus obtained:

$[\text{SiO}_2\text{@Au@SiO}_2]_{250,270,290}$: $r_1 = 250 \pm 10$ nm; $r_2 = 270 \pm 3$ nm;
 $r_3 = 290 \pm 3$ nm

$[\text{SiO}_2\text{@Au@SiO}_2]_{250,290,310}$: $r_1 = 250 \pm 10$ nm; $r_2 = 290 \pm 3$ nm;
35 $r_3 = 310 \pm 3$ nm

Protocol 9: Production of $[\text{SiO}_2\text{@Ag@SiO}_2]_{250,280,300}$ and

[SiO₂@Ag@SiO₂]_{250,290,310} nanospheres:

In a first step, silica nanospheres with a diameter of 50 nm to 300 nm were produced using the protocol described by W. Stöber, J. Colloid Interface Science, 26, 62 - 69, 1968 and Y. Zhang, Chinese Chem. Lett., 15, 8, 1005 - 1008, 2004 by introducing an ethanolic solution of tetraethoxysilane (TEOS) into a basic solution of 25% w/w ammonium hydroxide in a lower alcohol such as ethanol or a 3:1 mixture of propanol:methanol at ambient temperature and with mechanical agitation. The mixture was agitated for 1 h at ambient temperature and the silica colloids obtained were left to stand for 24 h. After evaporating off the ethanol and ammonia under reduced pressure, then washing with ethanol three times, SiO₂ nanospheres with a diameter of 250 ± 10 nm were obtained.

In a second step, the silica nanospheres obtained were mixed with a 1:9 water:ethanol solution containing silver nitrate AgNO₃ in a concentration of 0.1% under vigorous agitation. Next, an excess of an ethanolic solution of ammonium citrate was slowly introduced. The dispersion was left to stand for 24 h then centrifuged and washed with water three times to eliminate the residual reagents and to produce SiO₂@Ag nanospheres redispersed in 10 mL of water.

The SiO₂@Ag nanospheres thus obtained, placed in aqueous solution, were dispersed in pure ethanol at ambient temperature and with vigorous agitation. A 30% ammonium hydroxide solution and a solution of tetraethoxysilane (TEOS) were added to this dispersion simultaneously and with vigorous agitation over 1 h. The quantity of TEOS added was adjusted in order to control the thickness of the silica shell obtained around the SiO₂@Ag nanospheres.

After leaving overnight at 4°C, the SiO₂@Ag@SiO₂ nanospheres were centrifuged and washed several times with water and redispersed in 20 mL of water.

The following $\text{SiO}_2\text{@Ag@SiO}_2$ silica colloids were thus obtained:

- $[\text{SiO}_2\text{@Ag@SiO}_2]_{250,280,300}$: $r_1 = 250 \pm 10$ nm; $r_2 = 280 \pm 3$ nm;
 $r_3 = 300 \pm 3$ nm
- 5 $[\text{SiO}_2\text{@Ag@SiO}_2]_{250,290,310}$: $r_1 = 250 \pm 10$ nm; $r_2 = 290 \pm 3$ nm;
 $r_3 = 310 \pm 3$ nm

2nd step: Method for producing emissive composite materials with formula (II):

- 10 · Materials doped with fluorophores were obtained using the protocols described in the following publications:

- W.L. Vos, *J. Phys. Chem. B* 1999, 103 (9), pp 1408 - 1415; I. Sokolov, *Small* 2007, 3, 3, 419 - 4123;
15 *Small* 2008, 4, 7, 934 - 939; N. Halas, *Small* 2008, 4, 10, 1716 - 1722; A.E. Ostafin, *J. Non-Crystal Sol.* 2007, 353, 354 - 365; W.H. Tan, *Adv. Mater.* 2004, 16, 173 - 176; *Anal. Bioanal Chem.* 2006, 385, 518 - 524; *Nano Lett.* 2006, 6, 1, 84 - 88; *Langmuir* 2004, 20, 8336 - 8342;
20 *Langmuir* 2001, 17, 4812 - 4817; *J. Nanosci. Nanotechnol* 2002, 2, 405 - 409; J.Z. Zhou, *Anal. Chem.* 2004, 76, 5302 - 5312; D Levy, *Langmuir* 2000, 16, 7377 - 7382.

General protocol 10a:

- 25 (3-aminopropyl)triethoxysilane APTES was added to a suspension of $\text{SiO}_2\text{@Au@SiO}_2$ or $\text{SiO}_2\text{@Ag@SiO}_2$ nanospheres in deionized water, with vigorous agitation, at ambient temperature. After reacting for 30 minutes, the suspension of thus functionalized colloids was
30 centrifuged and washed three times with deionized water then taken up in suspension in deionized water. 5 equivalents of fluorophore dissolved in ethanol was then added dropwise to this aqueous suspension and at ambient temperature, with agitation for 30 minutes. After
35 leaving to stand for 24 h and at a temperature of 4°C, the suspension was centrifuged and washed several times

with a deionized water/ethanol mixture until the washing water was free of residual fluorophore.

General protocol 10b:

5 A phenyltriethoxysilane (PTES)/tetraethoxysilane (TEOS) mixture was added to a suspension of $\text{SiO}_2\text{@Au@SiO}_2$ or $\text{SiO}_2\text{@Ag@SiO}_2$ nanospheres in deionized water, with vigorous agitation at ambient temperature. After reacting for 30 minutes, the suspension of thus
10 functionalized colloids was centrifuged and washed three times with deionized water then taken up in suspension in deionized water. 5 equivalents of fluorophore dissolved in ethanol was then added dropwise to this aqueous suspension and at ambient temperature, with agitation for
15 30 minutes. After leaving to stand for 24 h and at a temperature of 4°C, the suspension was centrifuged and washed several times with a deionized water/ethanol mixture until the residual water was free of residual fluorophore.

20

General protocol 10c:

5 equivalents of a fluorophore dissolved in ethanol was added dropwise to a suspension of $\text{SiO}_2\text{@Au@SiO}_2$ or $\text{SiO}_2\text{@Ag@SiO}_2$ nanospheres in deionized water and at ambient
25 temperature and agitation was carried out for 30 minutes. After leaving to stand for 24 h and at a temperature of 4°C, the suspension was centrifuged and washed several times with a deionized water/ethanol mixture until the washing water was free of residual fluorophore.

30

The following fluorescent composite emissive
35 materials were obtained:

Ex11: [$\text{SiO}_2\text{@Ag@SiO}_2$ - 7-
hydroxy-4-

Ex12: [$\text{SiO}_2\text{@Au@SiO}_2$ - Cascade
yellow] 250, 270, 290

methylecoumarin] 250, 280, 300

Composition examples

The following compositions were prepared using conventional methods known to the skilled person with the particulate materials as described above. After application to the skin using the protocol described above, lightening was observed as follows, with:

- for example E1, a slightly yellow hue;
- for example E2, a slightly yellow hue;
- 10 • for example E3, a slightly red hue;
- for example E4, a slightly red hue;
- for example E5, a slightly beige hue.
- for example E6, a slightly red hue;
- for example E7, a slightly yellow hue;

15

Ingredients (% by weight)	E1	E2	E3	E4	E5	E6
2-OLEAMIDO-1,3-OCTADECANEDIOL	0.03	0.03	0.03	0.03	0.03	0.03
MAGNESIUM SULFATE	0.7	0.7	0.7	0.7	0.7	0.7
CHLORPHENESIN	0.25	0.25	0.25	0.25	0.25	0.25
METHYLPARABEN	0.25	0.25	0.25	0.25	0.25	0.25
BUTYLPARABEN	0.15	0.15	0.15	0.15	0.15	0.15
PHENOXYETHANOL	0.6	0.6	0.6	0.6	0.6	0.6
CYCLOPENTASILOXANE (and)						
DISTEARDIMONIUM HECTORITE (and)	5.82	5.82	5.82	5.82	5.82	5.82
ALCOHOL DENAT.						
DIMETHICONE	2.91	2.91	2.91	2.91	2.91	2.91
CYCLOPENTASILOXANE	10.35	10.35	10.35	10.35	10.35	10.35
ACETYLATED GLYCOL STEARATE	0.51	0.51	0.51	0.51	0.51	0.51

PROPYLENE GLYCOL	5	5	5	5	5	5
[Ag@SiO ₂ - Cascade Blue] _{40,60}	1.5				1.5	
[Ag@SiO ₂ - 7-hydroxy-4-methylcoumarin] _{40,60}		1.5				
[Ag@SiO ₂ - Cascade Yellow] _{80,100}	1	1	1.5	1.5	1.5	
[Ag@SiO ₂ - Alexa 488] _{80,100}						1.5
[Ag@SiO ₂ - Rhod-2] _{100,130}				1	1	1
[Ag@SiO ₂ - Cy3] _{100,130}			1			
ISODODECANE	1.88	1.88	1.88	1.88	1.88	1.88
WATER	62.5	62.5	62.5	62.5	61	61
POLYGLYCERYL-4 ISOSTEARATE (and)						
CETYL PEG/PPG-10/1 DIMETHICONE	6.55	6.55	6.55	6.55	6.55	6.55
(and) HEXYL LAURATE						
	100	100	100	100	100	100

Ingredients (% by weight)	E7
2-OLEAMIDO-1,3-OCTADECANEDIOL	0.03
MAGNESIUM SULFATE	0.7
CHLORPHENESIN	0.25
METHYLPARABEN	0.25
BUTYLPARABEN	0.15
PHENOXYETHANOL	0.6

CYCLOPENTASILOXANE (and) DISTEARDIMONIUM	
HECTORITE (and)	
ALCOHOL DENAT.	5.82
DIMETHICONE	2.91 5
CYCLOPENTASILOXANE	10.35
ACETYLATED GLYCOL STEARATE	0.51
PROPYLENE GLYCOL	5
[SiO ₂ @Ag@SiO ₂ - 7-hydroxy-4-methylcoumarin] _{250,280,300}	1.5 10
[SiO ₂ @Au@SiO ₂ - Cascade yellow] _{250,270,290}	1
ISODODECANE	1.88 15
WATER	62.5
POLYGLYCERYL-4 ISOSTEARATE (and)	
CETYL PEG/PPG-10/1 DIMETHICONE (and)	
HEXYL LAURATE	6.55 20
	100

The expression "comprising a" is synonymous with "comprising at least a".

CLAIMS

1. A cosmetic composition comprising:
 - a first fluorophore compound having an absorption spectrum; and
 - 5 • a second fluorophore compound having an emission spectrum overlapping the absorption spectrum of the first fluorophore compound, at least one of the two fluorophore compounds having luminescence enhanced by a proximity interaction effect with at least one
 - 10 metal, the metal and the fluorophore compound belonging to one and the same particle.
2. A composition according to claim 1, the first fluorophore compound having an enhanced luminescence
- 15 within a particle comprising the first fluorophore and a metal.
3. A composition according to claim 1 or claim 2, the second fluorophore compound having an enhanced
- 20 luminescence within a particle comprising the second fluorophore and a metal.
4. A composition according to any preceding claim, comprising a third fluorophore compound.
- 25 5. A composition according to the preceding claim, the third fluorophore compound having an enhanced luminescence within a particle comprising the third fluorophore and a metal.
- 30 6. A composition according to any preceding claim, the emission spectrum for the first fluorophore compound lying in the range 580 nm to 700 nm, preferably with a mid-height width for the emission curve of the first
- 35 fluorophore compound in the range 580 nm to 700 nm.

7. A composition according to any preceding claim, the emission spectrum for the second fluorophore compound lying in the range 480 nm to 620 nm, preferably with a mid-height width of the emission curve of the second fluorophore compound in the range 480 nm to 620 nm.
8. A composition according to any one of claims 1 to 7, the first fluorophore compound having an emission curve comprised at mid-height between 580 nm and 700 nm and an absorption curve in the visible comprised at mid-height between 480 nm and 620 nm, the second fluorophore compound having an emission curve comprised at mid-height between 480 nm and 620 nm.
9. A composition according to any one of claims 1 to 5, the first fluorophore compound having a normalized emission curve overlapping the relative luminous efficiency curve in the region 600 nm-700 nm.
10. A composition according to any one of claims 1 to 5, the first fluorophore compound having a normalized emission curve overlapping the relative luminous efficiency curve in the region 500 nm-600 nm.
11. A composition according to any one of claims 1 to 5, the second fluorophore compound having a normalized emission curve overlapping the relative luminous efficiency curve in the region 400 nm-500 nm.
12. A composition according to any one of claims 1 to 5, the first fluorophore compound having a normalized emission curve overlapping the relative luminous efficiency curve in the region 600 nm-700 nm and the second fluorophore compound has a normalized emission curve overlapping the relative luminous efficiency curve in the region 500 nm-600 nm.

13. A composition according to any preceding claim,
wherein the overlap of the absorption spectrum of the
first fluorophore compound and the emission spectrum
for the second fluorophore compound defines an area
the double of which is at least 50% of the sum of the
areas of said spectra.
14. A composition according to claim 4 or claim 5,
wherein:
- the third fluorophore compound emits fluorescent
light in the visible region such that the normalized
emission curve for the second fluorophore compound and
the relative luminous efficiency curve defined by the
CIE overlap each other in the wavelength region in the
range 400 nm to 500 nm;
 - the second fluorophore compound emits fluorescent
light in the visible region such that the normalized
emission curve for the second fluorophore compound and
the relative luminous efficiency curve defined by the
CIE overlap each other in the wavelength region in the
range 500 nm to 600 nm;
 - the first fluorophore emits fluorescent light in
the visible region such that the normalized emission
curve for the first fluorophore and the relative
luminous efficiency curve defined by the CIE overlap
each other in the wavelength region in the range
600 nm to 700 nm;
 - the absorption curve of the second fluorophore and
the emission curve of the third fluorophore overlap
each other; and
 - the absorption curve of the first fluorophore and
the emission curve of the second fluorophore overlap
each other when irradiated with natural light.
15. A composition according to any preceding claim, the
coverage of the composition being 70% or less,
preferably 65% or less, more preferably 60% or less.

16. A composition according to any preceding claim, the emission spectrum for the composition in the red having a peak that substantially coincides with the maximum sensitivity peak in the red of the human eye as defined by the CIE.
17. A composition according to any preceding claim, all of the fluorophore compounds being free of rare earths.
18. A composition according to any one of claims 1 to 17, the particle comprising a metallic core covered with a shell of a semi-organic or organic matrix containing the corresponding fluorophore compound, in particular a matrix of SiO_2 , PMMA, PVP, or PS.
19. A composition according to any one of claims 1 to 17, the particle comprising a non-metallic core covered with a layer of at least one metal, in particular gold or silver, and a shell of a matrix containing the corresponding fluorophore compound, in particular a silica matrix.
20. A composition according to claim 19, the core and the matrix being formed from the same substance, in particular silica.
21. A method of lightening the complexion, wherein a composition according to any preceding claim is applied to the skin, the covering power of the composition preferably being 70% or less, preferably 65% or less, more preferably 60% or less.
22. A method of modifying the tone of the skin, wherein a composition according to any one of claims 1 to 20 is applied to the skin, the covering power of the

composition being 70% or less, preferably 65% or less, more preferably 60% or less.

23. A method of lightening the complexion or for
5 modulating the tone of the skin, wherein a cosmetic composition comprising at least one fluorophore compound having enhanced fluorescence, in particular a compound comprising particles with a nanometric
10 metallic core and a coating covering the core, said coating comprising at least one fluorescent molecule disposed at the surface of the coating or impregnating it and located at a distance from the metallic core that is sufficiently small to increase the
15 fluorescence of the molecule is applied to the skin.
24. A method of enhancing the reflectance of skin in the wavelength region in the range 600 nm to 700 nm, comprising applying to the skin a cosmetic composition
20 comprising at least two fluorophore compounds F1 and F2 that are characterized in that the fluorophore compound F1 emits fluorescent light in the visible region such that the normalized emission curve for said fluorophore compound F1 and the relative luminous
25 efficiency curve defined by the CIE overlap each other in the wavelength region in the range 600 nm to 700 nm; and in that the absorption curve for the fluorophore F1 and the emission curve for the
30 fluorophore F2 overlap each other when irradiated with natural light.
25. A method of enhancing the reflectance of skin in the wavelength region in the range 500 nm to 600 nm, comprising applying to the skin a cosmetic composition
35 comprising at least two fluorophore compounds F3 and F4 that are characterized in that the fluorophore compound F4 emits fluorescent light in the visible region such that the normalized emission curve for the

fluorophore compound F4 and the relative luminous efficiency curve defined by the CIE overlap each other in the wavelength region in the range 500 nm to 600 nm; and in that the absorption curve for the fluorophore F4 and the emission curve for the fluorophore F3 overlap each other when irradiated with natural light.

26. A method of enhancing the reflectance of skin in the wavelength region in the range 500 nm to 700 nm, comprising applying to the skin a cosmetic composition comprising at least three fluorophore compounds F5, F6, and F7 that are characterized in that the fluorophore compound F5 emits fluorescent light in the visible region such that the normalized emission curve for the fluorophore compound F5 and the relative luminous efficiency curve defined by the CIE overlap each other in the wavelength region in the range 400 nm to 500 nm; in that the fluorophore compound F6 emits fluorescent light in the visible region such that the normalized emission curve for said fluorophore compound F6 and the relative luminous efficiency curve defined by the CIE overlap each other in the wavelength region in the range 500 nm to 600 nm; in that the fluorophore compound F7 emits fluorescent light in the visible region such that the normalized emission curve for the fluorophore compound F7 and the relative luminous efficiency curve defined by the CIE overlap each other in the wavelength region in the range 600 nm to 700 nm; in that the absorption curve for the fluorophore F6 and the emission curve for the fluorophore F5 overlap each other; and in that the absorption curve for the fluorophore F7 and the emission curve for the fluorophore F6 overlap each other when irradiated with natural light.

27. A method according to any one of claims 24 to 26, the overlap between the curves being such that twice the common area of the two overlapping curves represents at least 20%, preferably at least 30%, more preferably at least 40%, at least 50%, at least 60%, at least 70% or preferably at least 80% of the sum of the areas of each of said curves.

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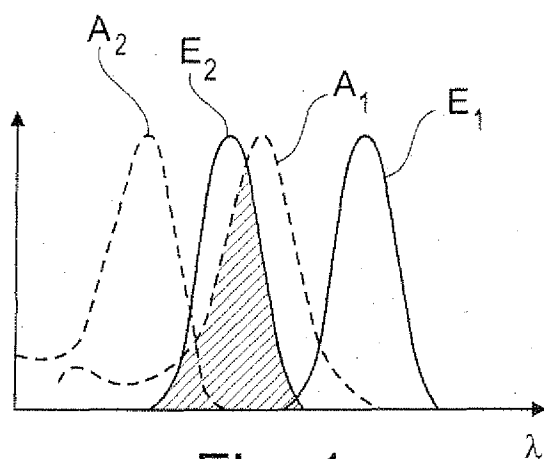


Fig. 1

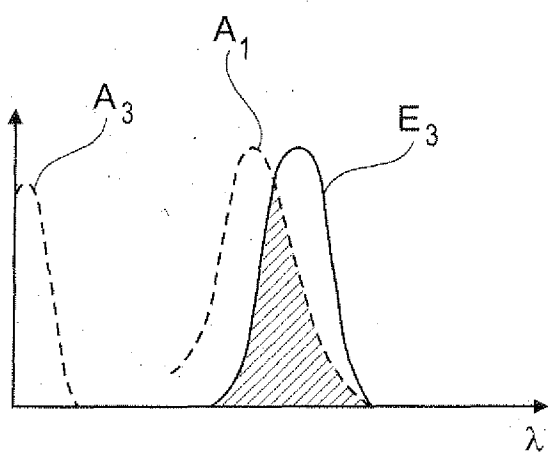


Fig. 2

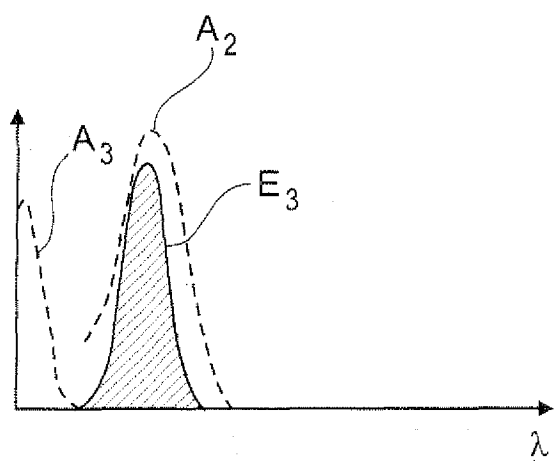


Fig. 3

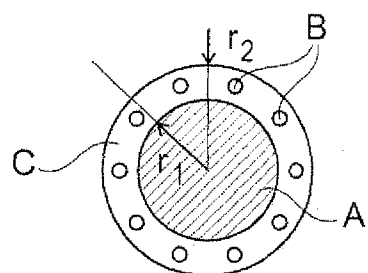


Fig. 4

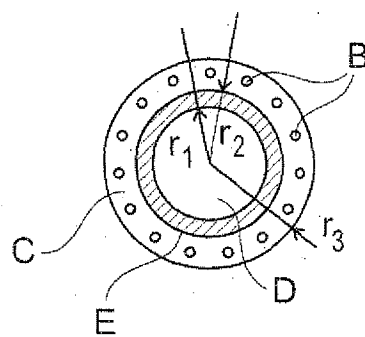


Fig. 5

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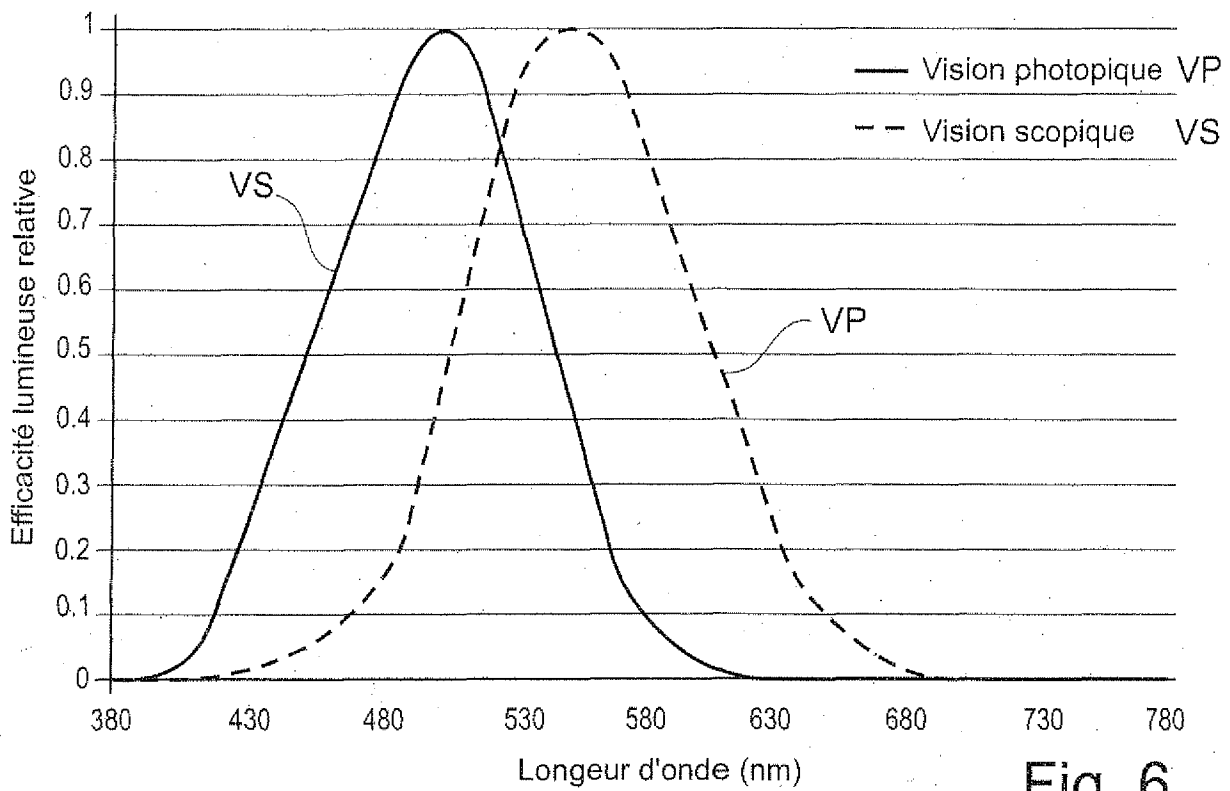


Fig. 6

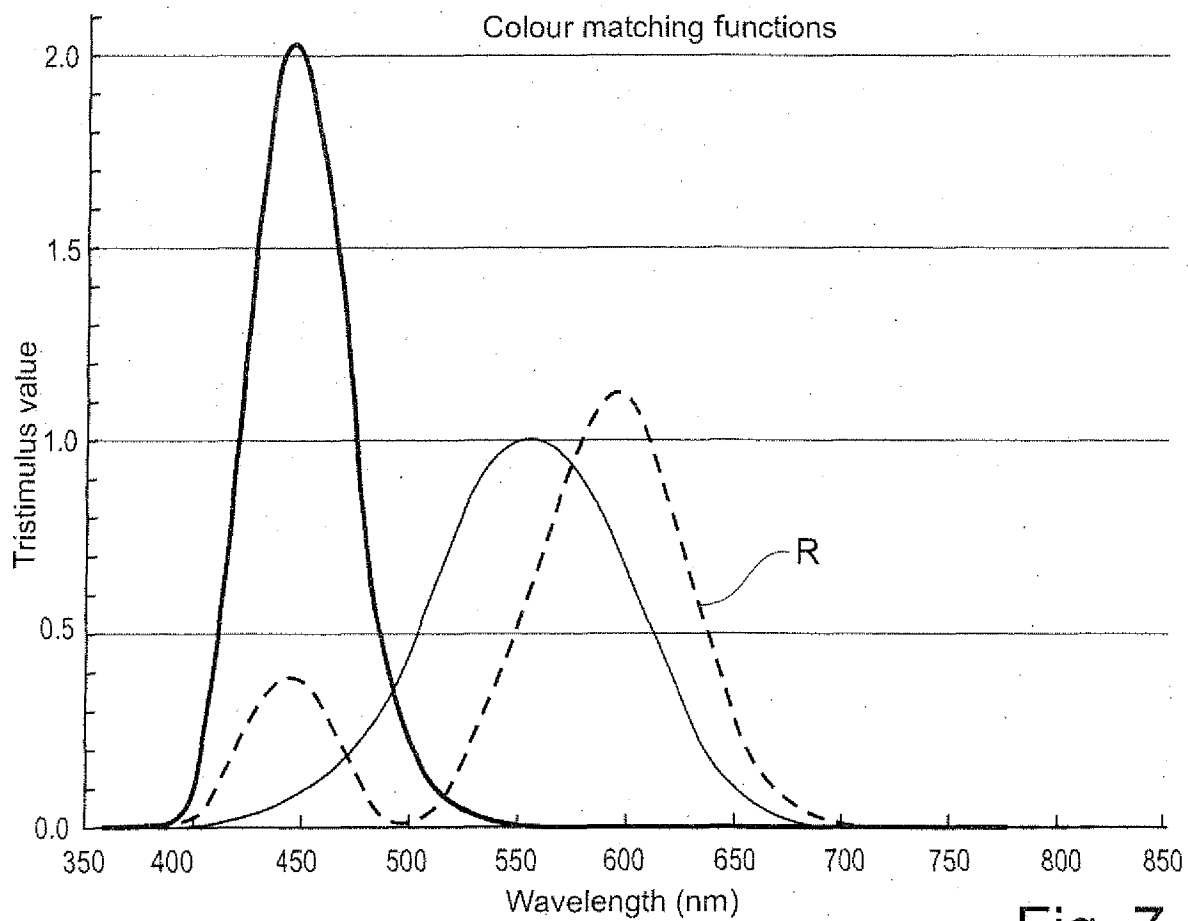


Fig. 7