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(71) Applicant *(for all designated States except AL)*: **L'OREAL** [FR/FR]; 14 rue Royale 75008 Paris (FR).

(72) Inventors; and
(71) Applicants *(for AL only)*: **BERNARD, Anne-Laure** [FR/FR]; c/o NIHON L'OREAL K.K., KSP R&D, 3-2-1, Sakado, Takatsu-ku, Kawasaki-shi, Kanagawa, 2130012 (JP). **IKEDA, Yuichi** [JP/JP]; c/o NIHON L'OREAL K.K., KSP R&D, 3-2-1, Sakado, Takatsu-ku, Kawasaki-shi, Kanagawa, 2130012 (JP).

(74) Agents: **MURAYAMA, Yasuhiko** et al.; 1-9-2, Marunouchi, Chiyoda-ku, Tokyo, 1006620 (JP).

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(54) **Title**: TRANSPARENT COMPOSITION CONTAINING OIL AND MICROCAPSULES

(57) **Abstract**: A transparent composition in the form of a nano- or micro-emulsion containing a microcapsule containing releasable colorant(s). The composition contains at least one fatty phase, at least one nonionic surfactant, at least one microcapsule containing releasable colorant(s), and water. This composition provides a high cosmeticity such as emolliency and high slipperiness while giving consumers a color change sensation upon shear.

DESCRIPTION

TITLE OF INVENTION

TRANSPARENT COMPOSITION CONTAINING OIL AND MICROCAPSULES

TECHNICAL FIELD

The present invention relates to a composition containing oil and microcapsules. More particularly, the present invention relates to a composition in a micro- or nano-emulsion comprising microcapsules containing a releasable colorant.

BACKGROUND ART

Cosmetic compositions are commonly used to give the skin an aesthetic color, but also to hide skin imperfections such as redness and/or marks. Many formulations have been developed to date. In addition, there is a growing interest in cosmetic products that provide a change in color in response to external incentives such as shear force.

Generally, this purpose is achieved by including in a composition microencapsulated colorants wherein, upon application on the skin, the composition provides a change of color. More particularly, the change of color is provided by the colorant-containing microcapsules, which upon rupture by application of a mechanical force, release the entrapped colorant into the composition, thereby changing its color. A mechanical action such as rubbing spreads the topical composition and facilitates its penetration into the skin. The immediate change of color of the composition provides a visual esthetic effect.

It has been known in the art to introduce pigments into cosmetic compositions, especially compositions for skin care or for making-up the skin containing a large amount of water. These compositions are expected to have a fresh sensorial effect on application, and to confer an appropriate color shade to the skin. Further, their ability to include large amounts of active ingredients is highly appreciated.

Such fresh sensorial and optical effects are for example needed in formulations of the "quick break type", in face serums, in eye serums and in foundations.

However, the introduction of a large amount of pigments may impair the fresh effect: the pigments tend to absorb water, leading the composition to dry out more rapidly, thus rendering the composition more difficult to apply uniformly on the skin.

As a consequence, the color of such a composition after application to the skin does not reach

the expected requirement regarding uniformity. Moreover it is not always possible to remedy this issue once the composition has formed a dry film on the skin.

In providing transparent cosmetics, the following technology has been used so far. It is a known practice, in the cosmetic or dermatological field, to use oil-in-water (O/W) emulsions. These emulsions, which consist of an oil phase (or lipophilic phase) dispersed in an aqueous phase, have an external aqueous phase. Therefore the products are more pleasant to use because of the freshness that they provide. However, they relatively lack stability when a large amount of oil is present. For some applications, it is advantageous to have a large amount of oils since the oils provide comfort for the skin, nourish it, and can also remove makeup from it when these oils have makeup-removing properties.

Moreover, it is advantageous to have fine emulsions, i.e., emulsions where the oil phase is in the form of very small droplets, i.e., of droplets less than 4 μm in size, since these fine emulsions have a pleasant cosmetic feel and are generally more stable than coarse emulsions.

These emulsions can be prepared in particular by the phase inversion temperature technique (PIT emulsions), in which the average size of the globules constituting the oil phase is within given limits, namely from 0.1 μm to 4 μm (100 nm to 4000 nm). The principle of phase inversion temperature (or PIT) emulsification is, in theoretical terms, well known to those skilled in the art; it was described in 1968 by K. Shinoda (J. Chem. Soc. Jpn., 1968, 89, 435). It was shown that this emulsification technique makes it possible to obtain stable fine emulsions (K. Shinoda and H. Saito, J. Colloid Interface Sci., 1969, 30, 258). This technology was applied in cosmetics as early as 1972 by Mitsui et al. ("Application of the phase-inversion-temperature method to the emulsification of cosmetics"; T. Mitsui, Y. Machida and F. Harusawa, American. Cosmet. Perfum., 1972, 87,33).

The principle of this technique is as follows: an O/W emulsion (introduction of the aqueous phase into the oil phase) is prepared at a temperature that is greater than the phase inversion temperature of the system, i.e., the temperature at which the equilibrium between the hydrophilic and lipophilic properties of the emulsifier(s) used is attained; at a higher temperature, i.e., greater than the phase inversion temperature (> PIT), the emulsion is of water-in-oil type and, as it cools, this emulsion inverts at the phase inversion temperature so as to become an emulsion of oil-in-water type, having beforehand passed through a state of micro-emulsion. This process makes it possible to readily obtain emulsions with a diameter generally less than 4 μm. Emulsifying surfactants of the oil-in-water type conventionally used have an HLB (hydrophilic lipophilic balance) ranging from 8 to 18. These emulsifiers, due to their amphiphilic structure, are situated at the oil phase/aqueous phase interface, and thus stabilize the dispersed oil droplets.

However, it is difficult to produce fine O/W emulsions containing a large amount of oil phase, since such emulsions have a tendency to destabilize, this destabilization resulting in coalescence and separation of the aqueous and oil phases with release of the oil. In order to improve the

stability of these emulsions, the concentration of emulsifiers can be increased; however, a high concentration of emulsifiers can result in a rough, clingy or sticky feel, and in problems of innocuousness with respect to the skin, the eyes and the scalp.

In particular, a fine emulsion such as an O/W nano- or micro-emulsion is of particular interest in cosmetic products due to its transparent or slightly translucent aspect.

For example, JP-A-H09-110635 discloses a fine emulsion which is formed by using a combination of polyglyceryl fatty acid ester, as a surfactant, and C_{10}-C_{22} 2-hydroxy fatty acid. In addition, JP-A-H11-71256 discloses a fine emulsion which is formed by using a combination of polyglyceryl fatty acid ester and a betain.

SUMMARY OF INVENTION

TECHNICAL PROBLEM

An objective of the present invention is to provide a composition with a large amount of oil with a transparent or slightly translucent, preferably transparent, aspect of the emulsion, having a color changing effect, and having a high degree of cosmeticity acceptable to many consumers.

SOLUTION OF PROBLEM

The above objective of the present invention can be achieved by a composition in the form of a nano- or micro-emulsion, containing (a) at least one fatty phase, (b) at least one nonionic surfactant, (c) at least one microcapsule containing releasable colorant(s), and (d) an aqueous phase.

BRIEF DESCRIPTION DRAWINGS

Drawings intended to illustrate the invention in a non-limitative way, representing examples of microcapsules to be introduced in a cosmetic composition according to the invention will be described as follows.

[Fig. 1] Figure 1 is a schematic diagram illustrating a typical structure of a color changing microcapsule of a first embodiment of the present invention, wherein A1 represents a core and B1, C1, D1 and E1 being different layers concentrically surrounding said core.

[Fig. 2] Figure 2 is a schematic diagram of the first embodiment of a microcapsule showing the core-shell structure of color-changing microcapsules B as used in Example 1 described below.

[Fig. 3] Figure 3 is a schematic diagram illustrating a typical structure of a microcapsule of a second embodiment of the present invention, wherein A2 represents a colored core, B2, C2, D2 and E2 being different layers concentrically surrounding the core A2, at least one of these

surrounding layers being mandatory and including preferably titanium dioxide particles, and the others being optional.

[Fig. 4] Figure 4 is a schematic diagram showing the core-shell structure of color-changing microcapsules of the second embodiment of a microcapsule containing 3 layers: colored core – inner color layer – TiO_2 particle layer. The pigment core included in the right particle of Fig. 4 corresponds to the left particle, which comprises a pigment/lecithin layer (inner color layer) and an inner pigment powder (inner colored core).

[Fig. 5] Figure 5 is a schematic diagram showing the core-shell structure of color-changing microcapsules of the second embodiment of a microcapsule containing 2 layers: colored core – TiO_2 particle layer.

DESCRIPTION OF EMBODIMENTS

Since the composition of the present invention can be transparent or slightly translucent, the composition can be preferably used for lotions and the like. As the dispersed phase is finely dispersed, the composition of the present invention can provide an emollient texture, as well as slipperiness. Furthermore, since the composition of the present invention contains microcapsules containing releasable colorant(s), the composition provides a color changing sensation upon application of shear or pressure by a consumer at the same time.

The composition of the present invention has a dispersed phase which has a smaller diameter due to the presence of at least one microcapsule containing a releasable colorant(s). Therefore, the composition can be in the form of a nano- or micro-emulsion with transparency or slight translucency.

Hereinafter, the composition of the present invention will be explained in a more detailed manner.

1-1. FATTY PHASE

The composition of the present invention contains at least one fatty phase mainly consisting of oil. Here, "oil" means a fatty compound or substance which is in the form of a liquid at room temperature (25°C) under atmospheric pressure (760 mmHg). Those oils generally used in cosmetics can be used alone or in combination thereof. These oils may be volatile or non-volatile, preferably non-volatile. The oil may be a polar oil or a non-polar oil.

The oil may be a synthetic oil or a naturally-derived oil, such as plant oil, and animal oil.

The plant oils may include, for example, linseed oil, camellia oil, macadamia nut oil, corn oil, mink oil, olive oil, avocado oil, sasanqua oil, castor oil, safflower oil, jojoba oil, sunflower oil, almond oil, rapeseed oil, sesame oil, soybean oil and peanut oil.

The animal oils may include, for example, squalene and squalane.

The oil may be a hydrocarbon oil, a silicone oil, or a fluoro oil. The hydrocarbon oil may include an alkane oil, an ester oil, an ether oil, and a triglyceride oil.

The ester oils are preferably liquid esters of saturated or unsaturated, linear or branched C_1-C_{26} aliphatic monoacids or polyacids and of saturated or unsaturated, linear or branched C_1-C_{26} aliphatic monoalcohols or polyalcohols, the total number of carbon atoms of the esters being greater than or equal to 10. Preferably, for the esters of monoalcohols, at least one of the alcohol moiety and the acid moiety from the esters is branched. Among the monoesters of monoacids and monoalcohols, mention may be made of ethyl palmitate, ethyl hexyl palmitate, isopropyl palmitate, dicaprylyl carbonate, alkyl myristates such as isopropyl myristate or ethyl myristate, isocetyl stearate, 2-ethylhexyl isononanoate, isononyl isononanoate, isodecyl neopentanoate and isostearyl neopentanoate. Esters of C_4-C_{22} dicarboxylic or tricarboxylic acids and of C_1-C_{22} alcohols and esters of monocarboxylic, dicarboxylic or tricarboxylic acids and of non-sugar C_4-C_{26} dihydroxy, trihydroxy, tetrahydroxy or pentahydroxy alcohols may also be used. Mention may especially be made of: diethyl sebacate; isopropyl lauroyl sarcosinate; diisopropyl sebacate; bis(2-ethylhexyl) sebacate; diisopropyl adipate; di-n-propyl adipate; dioctyl adipate; bis(2-ethylhexyl) adipate; diisostearyl adipate; bis(2-ethylhexyl) maleate; triisopropyl citrate; triisocetyl citrate; triisostearyl citrate; glyceryl trilactate; glyceryl trioctanoate; trioctyldodecyl citrate; trioleyl citrate; neopentyl glycol diheptanoate; diethylene glycol diisononanoate. As ester oils, one can use sugar esters and diesters of C_6-C_{30} and preferably C_{12}-C_{22} fatty acids. The term "sugar" means oxygen-bearing hydrocarbon-based compounds containing several alcohol functions, with or without aldehyde or ketone functions, and which contain at least 4 carbon atoms. These sugars may be monosaccharides, oligosaccharides or polysaccharides. Examples of suitable sugars that may be mentioned include sucrose (or saccharose), glucose, galactose, ribose, fucose, maltose, fructose, mannose, arabinose, xylose and lactose, and derivatives thereof, especially alkyl derivatives, such as methyl derivatives, for example, methylglucose. The sugar esters of fatty acids may be selected especially from the group containing the esters or mixtures of esters of sugars described previously and of linear or branched, saturated or unsaturated C_6-C_{30} and preferably C_{12}-C_{22} fatty acids. If they are unsaturated, these compounds may have one to three conjugated or non-conjugated carbon-carbon double bonds. The esters may also be selected from the group consisting of monoesters, diesters, triesters, tetraesters and polyesters, and mixtures thereof. These esters may be, for example, oleates, laurates, palmitates, myristates, behenates, cocoates, stearates, linoleates, linolenates, caprates and arachidonates, or mixtures thereof such as, especially, oleopalmitate, oleostearate and palmitostearate mixed esters, as well as pentaerythrityl tetraethyl hexanoate. More particularly, use is made of monoesters and diesters and especially sucrose, glucose or methylglucose monooleates or dioleates, stearates, behenates, oleopalmitates, linoleates, linolenates and oleostearates. An example that may be mentioned is the product sold under the name Glucate® DO by the company Amerchol, which is a methylglucose dioleate. As examples of preferable ester oils, mention may be made of, for example, diisopropyl adipate, dioctyl adipate, 2-ethylhexyl hexanoate, ethyl laurate, cetyl

octanoate, octyldodecyl octanoate, isodecyl neopentanoate, myristyl propionate, 2-ethylhexyl 2-ethylhexanoate, 2-ethylhexyl octanoate, 2-ethylhexyl caprylate/caprate, methyl palmitate, ethyl palmitate, isopropyl palmitate, ethylhexyl palmitate, isohexyl laurate, hexyl laurate, isocetyl stearate, isopropyl isostearate, isopropyl myristate, isodecyl oleate, glyceryl tri(2-ethylhexanoate), pentaerythrithyl tetra(2-ethylhexanoate), 2-ethylhexyl succinate, diethyl sebacate, and mixtures thereof.

The triglycerides may include artificial triglycerides, for example, glyceryl trimyristate, glyceryl tripalmitate, glyceryl trilinolenate, glyceryl trilaurate, glyceryl tricaprate, glyceryl tricaprylate, glyceryl tri(caprate/caprylate) and glyceryl tri(caprate/caprylate/linolenate).

As silicone oils, mention may be made of, for example, linear organopolysiloxanes such as dimethylpolysiloxane, methylphenylpolysiloxane, methylhydrogenpolysiloxane, and the like; cyclic organopolysiloxanes such as octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, dodecamethylcyclohexasiloxane, and the like; and mixtures thereof. Preferably, silicone oil is chosen from liquid polydialkylsiloxanes, especially liquid polydimethylsiloxanes (PDMS) and liquid polyorganosiloxanes containing at least one aryl group. These silicone oils may also be organomodified. The organomodified silicones that can be used in accordance with the present invention are silicone oils as defined above and containing in their structure one or more organofunctional groups attached via a hydrocarbon-based group. Organopolysiloxanes are defined in greater detail in Walter Noll's *Chemistry and Technology of Silicones* (1968), Academic Press. They may be volatile or non-volatile. Volatile or non-volatile silicone oils, such as volatile or non-volatile polydimethylsiloxanes (PDMS) containing a linear or cyclic silicone chain, that are liquid or pasty at ambient temperature, in particular cyclopolydimethylsiloxanes (cyclomethicones) such as cyclohexasiloxane; polydimethylsiloxanes containing alkyl, alkoxy or phenyl groups that are pendent or at the end of the silicone chain, which groups have from 2 to 24 carbon atoms; phenyl silicones such as phenyl trimethicones, phenyl dimethicones, phenyltrimethylsiloxydiphenylsiloxanes, diphenyl dimethicones, diphenylmethyldiphenyltrisiloxanes, 2-phenylethyltrimethyl siloxysilicates, and polymethylphenylsiloxanes, may be used.

The alkane oils may be chosen from:

- linear or branched, optionally cyclic, C_6-C_{16} lower alkanes. Examples that may be mentioned include hexane, undecane, dodecane, tridecane, and isoparaffins, for instance isohexadecane, isododecane and isodecane; and
- linear or branched hydrocarbons containing more than 16 carbon atoms, such as liquid paraffins, liquid petroleum jelly, polydecenes and hydrogenated polyisobutenes such as Parleam®, and squalane.

Preferably, the alkane oils may include, linear or branched hydrocarbons such as mineral oil (e.g., liquid paraffin), paraffin, Vaseline or petrolatum, naphthalenes, and the like; hydrogenated polyisobutene, isoeicosan, and decene/butene copolymer; and mixtures thereof. Preferably the

oil may be chosen from hydrocarbon oils in the form of a liquid at room temperature under atmospheric pressure.

Preferably, the oil has a low molecular weight such as below 700 g/mol, chosen from ester oils with a short hydrocarbon chain(s) (C_1-C_{12}) (e.g., isopropyl myristate, isopropyl palmitate, isononyl isononanoate, and ethyl hexyl palmitate), hydrocarbon oils (e.g., isododecane, isohexadecane, and squalane), branched and/or unsaturated fatty alcohol (C_{12}-C_{30}) type oils such as octyldodecanol, oleyl alcohol, and ether oils such as dicaprylyl ether.

The oil may be selected from the group consisting of plant oils, animal oils, mineral oils, synthetic oils, silicone oils and hydrocarbon oils, preferably hydrocarbon oils selected from the group consisting of ester oil, ether oil, alkane oil, and triglyceride oil.

The amount of the oil in the composition of the present invention is not limited, and may range from 0.1% to 50% by weight, preferably from 0.5% to 40% by weight, and more preferably from 5% to 30% by weight, relative to the total weight of the composition.

1-2. NONIONIC SURFACTANT

The composition of the present invention contains at least one nonionic surfactant. A single type of nonionic surfactant may be used, but two or more different types of nonionic surfactants may be used in combination.

The nonionic surfactant is not limited, but may have an HLB (Hydrophilic Lipophilic Balance) value of from 8.0 to 14.0, preferably from 9.0 to 13.5, and more preferably from 10.0 to 13.0. If two or more nonionic surfactants are used, the HLB value is determined by the weight average of the HLB values of all the nonionic surfactants.

The nonionic surfactant may be chosen from:

(1) surfactants that are fluid at a temperature of less than or equal to 45°C, chosen from the esters of at least one polyol chosen from the group formed by polyethylene glycol containing from 1 to 60 ethylene oxide units, sorbitan, glycerol containing from 2 to 30 ethylene oxide units, polyglycerols containing from 2 to 12 glycerol units, and of at least one fatty acid containing at least one saturated or unsaturated, linear or branched C_8-C_{22} alkyl chain,
(2) mixed esters of fatty acid or of fatty alcohol, of carboxylic acid and of glycerol,
(3) fatty acid esters of sugars and fatty alcohol ethers of sugars,
(4) surfactants that are solid at a temperature of less than or equal to 45°C, chosen from fatty esters of glycerol, fatty esters of sorbitan and oxyethylenated fatty esters of sorbitan, ethoxylated fatty ethers and ethoxylated fatty esters,
(5) block copolymers of ethylene oxide (A) and of propylene oxide (B), and
(6) silicone surfactants.

The (1) surfactants that are fluid at a temperature of less than or equal to 45°C may be, in

particular:

- the isostearate of polyethylene glycol of molecular weight 400, sold under the name PEG 400 by the company Unichema;
- diglyceryl isostearate, sold by the company Solvay;
- glyceryl laurate containing 2 glycerol units, sold by the company Solvay;
- sorbitan oleate, sold under the name Span 80 by the company ICI;
- sorbitan isostearate, sold under the name Nikkol SI 10R by the company Nikko; and
- α-butylglucoside cocoate or α-butylglucoside caprate, sold by the company Ulice.

The (2) mixed esters of fatty acid or of fatty alcohol, of carboxylic acid and of glycerol, which can be used as the above nonionic surfactant, may be chosen in particular from the group containing mixed esters of fatty acid or of fatty alcohol with an alkyl chain containing from 8 to 22 carbon atoms, and of α-hydroxy acid and/or of succinic acid, with glycerol. The α-hydroxy acid may be, for example, citric acid, lactic acid, glycolic acid or malic acid, and mixtures thereof.

The alkyl chain of the fatty acids or alcohols from which are derived the mixed esters which can be used in the nano-emulsion of the present invention may be linear or branched, and saturated or unsaturated. They may especially be stearate, isostearate, linoleate, oleate, behenate, arachidonate, palmitate, myristate, laurate, caprate, isostearyl, stearyl, linoleyl, oleyl, behenyl, myristyl, lauryl or capryl chains, and mixtures thereof.

As examples of mixed esters which can be used in the nano-emulsion of the present invention, mention may be made of the mixed ester of glycerol and of the mixture of citric acid, lactic acid, linoleic acid and oleic acid (CTFA name: Glyceryl citrate / lactate / linoleate / oleate) sold by the company Hüls under the name Imwitor 375; the mixed ester of succinic acid and of isostearyl alcohol with glycerol (CTFA name: Isostearyl diglyceryl succinate) sold by the company Hüls under the name Imwitor 780 K; the mixed ester of citric acid and of stearic acid with glycerol (CTFA name: Glyceryl stearate citrate) sold by the company Hüls under the name Imwitor 370; the mixed ester of lactic acid and of stearic acid with glycerol (CTFA name: Glyceryl stearate lactate) sold by the company Danisco under the name Lactodan B30 or Rylo LA30.

The (3) fatty acid esters of sugars, which can be used as the above nonionic surfactant, may preferably be solid at a temperature of less than or equal to 45°C and may be chosen in particular from the group containing esters or mixtures of esters of C_8-C_{22} fatty acid and of sucrose, of maltose, of glucose or of fructose, and esters or mixtures of esters of C_{14}-C_{22} fatty acid and of methylglucose.

The C_8-C_{22} or C_{14}-C_{22} fatty acids forming the fatty unit of the esters contain a saturated or unsaturated linear alkyl chain containing, respectively, from 8 to 22 or from 14 to 22 carbon atoms. The fatty unit of the esters may be chosen in particular from stearates, behenates, arachidonates, palmitates, myristates, laurates and caprates, and mixtures thereof. Stearates are

preferably used.

As examples of esters or mixtures of esters of fatty acid and of sucrose, of maltose, of glucose or of fructose, mention may be made of sucrose monostearate, sucrose distearate and sucrose tristearate and mixtures thereof, such as the products sold by the company Croda under the name Crodesta F50, F70, F110 and F160; and examples of esters or mixtures of esters of fatty acid and of methylglucose which may be mentioned are methylglucose polyglyceryl-3 distearate, sold by the company Goldschmidt under the name Tego-care 450. Mention may also be made of glucose or maltose monoesters such as methyl o-hexadecanoyl-6-D-glucoside and o-hexadecanoyl-6-D-maltoside.

The (3) fatty alcohol ethers of sugars, which can be used as the above nonionic surfactant, may be solid at a temperature of less than or equal to 45°C and may be chosen in particular from the group containing ethers or mixtures of ethers of C_8-C_{22} fatty alcohol and of glucose, of maltose, of sucrose or of fructose, and ethers or mixtures of ethers of a C_{14}-C_{22} fatty alcohol and of methylglucose. These are in particular alkylpolyglucosides.

The C_8-C_{22} or C_{14}-C_{22} fatty alcohols forming the fatty unit of the ethers which may be used in the nanoemulsion of the present invention contain a saturated or unsaturated, linear alkyl chain containing, respectively, from 8 to 22 or from 14 to 22 carbon atoms. The fatty unit of the ethers may be chosen in particular from decyl, cetyl, behenyl, arachidyl, stearyl, palmityl, myristyl, lauryl, capryl and hexadecanoyl units, and mixtures thereof, such as cetearyl.

As fatty alcohol ethers of sugars, for example, mention may be made of alkylpolyglucosides such as decylglucoside and laurylglucoside, which is sold, for example, by the company Henkel under the respective names Plantaren 2000 and Plantaren 1200, cetostearyl glucoside optionally as a mixture with cetostearyl alcohol, sold for example, under the name Montanov 68 by the company SEPPIC, under the name Tego-care CG90 by the company Goldschmidt and under the name Emulgade KE3302 by the company Henkel, as well as arachidyl glucoside, for example in the form of a mixture of arachidyl alcohol and behenyl alcohol and arachidyl glucoside, sold under the name Montanov 202 by the company SEPPIC.

The surfactant used more particularly is sucrose monostearate, sucrose distearate or sucrose tristearate and mixtures thereof, methylglucose polyglyceryl-3 distearate and alkylpolyglucosides.

The (4) fatty esters of glycerol which may be used as the above nonionic surfactant, which are solid at a temperature of less than or equal to 45°C, may be chosen in particular from the group containing esters formed from at least one acid containing a saturated linear alkyl chain containing from 12 to 22 carbon atoms and from 1 to 12 glycerol units. One or more of these fatty esters of glycerol may be used in the present invention.

These esters may be chosen in particular from stearates, behenates, arachidates and palmitates,

and mixtures thereof. Stearates and palmitates are more preferably used.

As surfactants which can be used in the present invention, for example, mention may be made of decaglyceryl monostearate, distearate, tristearate and pentastearate (CTFA names: Polyglyceryl-10 stearate, Polyglyceryl-10 distearate, Polyglyceryl-10 tristearate, Polyglyceryl-10 pentastearate), such as the products sold under the respective names Nikkol Decaglyn 1-S, 2-S, 3-S and 5-S by the company Nikko, and diglyceryl monostearate (CTFA name: Polyglyceryl-2 stearate), such as the product sold by the company Nikko under the name Nikkol DGMS.

The (4) fatty esters of sorbitan which may be used as the above nonionic surfactant, which are solid at a temperature of less than or equal to 45°C, may be chosen from the group containing C_{16}-C_{22} fatty acid esters of sorbitan and oxyethylenated C_{16}-C_{22} fatty acid esters of sorbitan. They are formed from at least one fatty acid containing at least one saturated linear alkyl chain containing, respectively, from 16 to 22 carbon atoms, and from sorbitol or from ethoxylated sorbitol. The oxyethylenated esters generally contain from 1 to 100 ethylene glycol units and preferably from 2 to 40 ethylene oxide (EO) units.

These esters may be chosen in particular from stearates, behenates, arachidates, palmitates, and mixtures thereof. Stearates and palmitates are preferably used.

As examples of the above nonionic surfactant that can be used in the present invention, mention may be made of sorbitan monostearate (CTFA name: Sorbitan stearate), sold by the company ICI under the name Span 60, sorbitan monopalmitate (CTFA name: Sorbitan palmitate), sold by the company ICI under the name Span 40, and sorbitan tristearate 20 EO (CTFA name: Polysorbate 65), sold by the company ICI under the name Tween 65.

The (4) ethoxylated fatty ethers that are solid at a temperature of less than or equal to 45°C, which may be used as the above nonionic surfactant, are preferably ethers formed from 1 to 100 ethylene oxide units and from at least one fatty alcohol chain containing from 16 to 22 carbon atoms. The fatty chain of the ethers may be chosen in particular from behenyl, arachidyl, stearyl and cetyl units, and mixtures thereof, such as cetearyl. Examples of ethoxylated fatty ethers which may be mentioned are behenyl alcohol ethers containing 5, 10, 20 and 30 ethylene oxide units (CTFA names: Beheneth-5, Beheneth-10, Beheneth-20, Beheneth-30), such as the products sold under the names Nikkol BB5, BB10, BB20 and BB30 by the company Nikko, and stearyl alcohol ether containing 2 ethylene oxide units (CTFA name: Steareth-2), such as the product sold under the name Brij 72 by the company ICI.

The (4) ethoxylated fatty esters that are solid at a temperature of less than or equal to 45°C, which may be used as the above nonionic surfactant, are esters formed from 1 to 100 ethylene oxide units and from at least one fatty acid chain containing from 16 to 22 carbon atoms. The fatty chain in the esters may be chosen in particular from stearate, behenate, arachidate and palmitate units, and mixtures thereof. Examples of ethoxylated fatty esters which may be

mentioned are the ester of stearic acid containing 40 ethylene oxide units, such as the product sold under the name Myrj 52 (CTFA name: PEG-40 stearate) by the company ICI, as well as the ester of behenic acid containing 8 ethylene oxide units (CTFA name: PEG-8 behenate), such as the product sold under the name Compritol HD5 ATO by the company Gattefosse.

The (5) block copolymers of ethylene oxide (A) and of propylene oxide (B), which may be used as surfactants in the nanoemulsion according to the present invention, may be chosen in particular from block copolymers of formula (I):

[formula (I)]

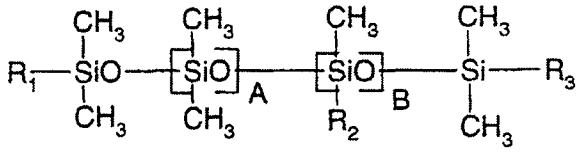
$$HO(C_2H_4O)_x(C_3H_6O)_y(C_2H_4O)_zH \qquad (I)$$

in which x, y and z are integers such that x+z ranges from 2 to 100 and y ranges from 14 to 60, and mixtures thereof, and more particularly from the block copolymers of formula (IV) having an HLB value ranging from 8.0 to 14.

As (6) silicone surfactants which can be used according to the present invention, for example, mention may be made of those disclosed in documents US-A-5364633 and US-A-5411744.

The (6) silicone surfactant as the above nonionic surfactant may preferably be a compound of formula (II):

[formula (II)]



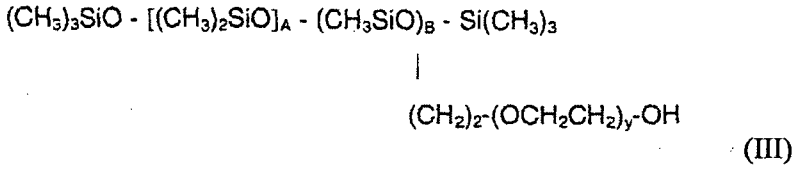
(II)

in which:
R_1, R_2 and R_3, independently of each other, represent a C_1-C_6 alkyl radical or a radical $-(CH_2)_x-(OCH_2CH_2)_y-(OCH_2CH_2CH_2)_z-OR_4$, at least one radical R_1, R_2 or R_3 not being an alkyl radical; R_4 being a hydrogen, an alkyl radical or an acyl radical;
A is an integer ranging from 0 to 200;
B is an integer ranging from 0 to 50; with the proviso that A and B are not simultaneously equal to zero;
x is an integer ranging from 1 to 6;
y is an integer ranging from 1 to 30;
z is an integer ranging from 0 to 5.

In a preferred embodiment, in the compound of formula (II), the alkyl radical is a methyl radical, x is an integer ranging from 2 to 6 and y is an integer ranging from 4 to 30.

As silicone surfactants of formula (II), for example, mention may be made of the compounds of formula (III):

[formula (III)]

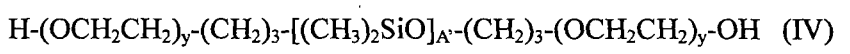


(III)

in which A is an integer ranging from 20 to 105, B is an integer ranging from 2 to 10 and y is an integer ranging from 10 to 20.

As examples of silicone surfactants of formula (II), mention may also be made of the compounds of formula (IV):

[formula (IV)]



(IV)

in which A' and y are integers ranging from 10 to 20.

Compounds of the present invention which may be used are those sold by the company Dow Corning under the names DC 5329, DC 7439-146, DC 2-5695 and Q4-3667. The compounds DC 5329, DC 7439-146 and DC 2-5695 are compounds of formula (II) in which, respectively, A is 22, B is 2 and y is 12; A is 103, B is 10 and y is 12; A is 27, B is 3 and y is 12.

The compound Q4-3667 is a compound of formula (III) in which A is 15 and y is 13.

Preferably, the nonionic surfactant may be chosen from:
- polyethylene glycol isostearate or oleate (8 to 10 mol of ethylene oxide),
- polyethylene glycol isocetyl, behenyl ether or isostearyl ether (8 to 10 mol of ethylene oxide),
- polyglyceryl monolaurate or dilaurate containing 3 to 6 glycerol units,
- polyglyceryl mono(iso)stearate containing 3 to 6 glycerol units,
- polyglyceryl monooleate containing 3 to 6 glycerol units, and
- polyglyceryl dioleate containing 3 to 6 glycerol units.

Preferably, the nonionic surfactant is selected from polyglyceryl fatty acid esters and mono- or poly-oxyalkylenated fatty acid esters.

Preferably, the polyglyceryl fatty acid ester contains esters of a fatty acid and polyglycerine

containing 70% or more of polyglycerine whose polymerization degree is 4 or more, preferably esters of a fatty acid and polyglycerine containing equal to or more than 60% of polyglycerine whose polymerization degree is between 4 and 11, and more preferably esters of a fatty acid and polyglycerine containing equal to or more than 30% of polyglycerine whose polymerization degree is 5.

The polyglyceryl fatty acid ester may be chosen from the mono-, di- and triesters of saturated or unsaturated acid, preferably saturated acid, including 2 to 30 carbon atoms, preferably 6 to 30 carbon atoms, and more preferably 8 to 30 carbon atoms, such as lauric acid, oleic acid, stearic acid, isostearic acid, capric acid, caprylic acid, and myristic acid.

The polyglyceryl fatty acid ester may have a polyglyceryl moiety derived from 2 to 10 glycerols, more preferably from 3 or 4 to 6 glycerols, and further more preferably 5 or 6 glycerols.

Preferably, the polyglyceryl (PG) fatty acid ester may be selected from the group consisting of PG-4 laurate, PG-5 laurate, PG-5 dilaurate, PG-5 oleate, PG-5 dioleate, PG-6 tricaprylate, PG-5 myristate, PG-5 trimyristate, PG-5 stearate, PG-5 isostearate, PG-5 trioleate, PG-6 caprylate, and PG-6 tricaprylate.

Preferably, the mono- or poly-oxyalkylenated fatty acid ester has a (poly)oxyalkylene moiety derived from 1 to 20 oxyalkylenes, preferably from 3 to 15 oxyalkylenes, and more preferably 8 to 10 oxyalkylenes.

The oxyalkylene moiety may be derived from alkylene glycols such as ethyleneglycol, propylene glycol, butyleneglycol, pentyleneglycol, hexyleneglycol, and the like. The oxyalkylene moiety may contain a number of moles of ethylene oxide and/or of propylene oxide of between 1 and 100 and preferably between 2 and 50. Advantageously, the nonionic surfactants do not contain any oxypropylene units.

The mono- or poly-oxyalkylenated fatty acid ester may be chosen from the mono- and diesters of saturated or unsaturated acid, preferably saturated acid, including 2 to 30 carbon atoms, preferably 6 to 30 carbon atoms, and more preferably 8 to 30 carbon atoms, such as lauric acid, oleic acid, stearic acid, isostearic acid, capric acid, caprylic acid, and myristic acid.

Examples of mono- or poly-oxyalkylenated fatty acid esters that may be mentioned include esters of saturated or unsaturated, linear or branched, C_2-C_{30}, preferably C_6-C_{30} and more preferably C_8-C_{22} acids and of polyethylene glycols.

Examples of mono- or poly-oxyalkylenated fatty acid esters that may be mentioned include the adducts of ethylene oxide with esters of lauric acid, myristic acid, palmitic acid, stearic acid, isostearic acid, oleic acid or behenic acid, and mixtures thereof, especially those containing from 8 to 20 oxyethylene groups, such as PEG-8 to PEG-20 laurate (as the CTFA names: PEG-8 laurate to PEG-20 laurate); PEG-8 to PEG-20 myristate (as the CTFA names: PEG-8 mysistate

to PEG-20 mysistate); PEG-8 to PEG-20 palmitate (as the CTFA names: PEG-8 palmitate to PEG-20 palmitate); PEG-8 to PEG-20 stearate (as the CTFA names: PEG-8 stearate to PEG-20 stearate); PEG-8 to PEG-20 isostearate (as the CTFA names: PEG-8 isostearate to PEG-20 isostearate); PEG-8 to PEG-20 oleate (as the CTFA names: PEG-8 oleate to PEG-20 oleate); PEG-8 to PEG-20 behenate (as the CTFA names: PEG-8 behenate to PEG-20 behenate); and mixtures thereof.

Preferably, the polyglycol fatty acid ester may be selected from the group consisting of PEG-8 isostearate, PEG-8 stearate, PEG-10 isostearate, PEG-10 oleate, PEG-10 isocetyl ether, PEG-10 behenyl ether or PEG-10 isostearyl ether and a mixture thereof. Preferred nonionic surfactants are polyglyceryl (PG) fatty acid esters.

Preferably, the nonionic surfactant may be selected from the group consisting of mono- or polyoxyalkylenated fatty acid esters, a polyglyceryl fatty ester surfactant, and fatty acid esters of sugars, especially of sucrose.

The amount of the nonionic surfactant in the composition of the present invention is not limited, and may range from 0.1% to 30% by weight, preferably from 0.5% to 15% by weight, and more preferably from 1% to 10% by weight, relative to the total weight of the composition.

1-3. AQUEOUS PHASE

The composition of the present invention contains at least one aqueous phase. The aqueous phase contains water as main component. The amount of water is not limited, and may be from 5% to 99% by weight, preferably from 10% to 95% by weight, and more preferably from 15% to 90% by weight, relative to the total weight of the composition.

The aqueous phase may further contain at least one organic solvent, preferably water-miscible organic solvent. As the organic solvent, there may be mentioned, for example, C_1-C_4 alkanols, such as ethanol and isopropanol; aromatic alcohols such as benzyl alcohol and phenoxyethanol; analogous products thereof; and mixtures thereof. The amount of the organic water-miscible solvent may be less than 10% by weight, preferably 5% by weight or less, and more preferably 1% by weight or less, relative to the total weight of the composition.

1-4. MICROSCAPSULE CONTAINING A RELEASABLE COLORANT

The term "microcapsule", as used herein, refers to a spherical microcapsule containing at least one layered coating entrapping at least one colorant and surrounding a core chemically different from the coating. Microcapsules are distinct from microspheres, which consist of a spherical homogeneous matrix.

In an embodiment, the “at least one layered coating” is a multilayered coating preferably an organic multilayered coating.

The term "multilayered microcapsule" refers to a microcapsule consisting of a core surrounded

by a coating based on one or more inner layer(s) and one outer layer. The one or more inner layer(s) forming the multilayered coating of the multilayered microcapsule and the single outer layer of the microcapsule may be formed of the same or different wall-forming organic compound(s).

The microcapsule contains a core also called an "inner core" surrounded by a coating based on one or more layer(s). In a preferred embodiment, the microcapsule is a 'multilayered' microcapsule, containing at least one inner layer and one outer layer. The one or more inner layer(s) forming the multi-layer coating of the multilayered microcapsule and the single outer layer of the microcapsule may be formed of the same or different wall-forming organic compound(s).

In a particular embodiment, the inner layer and the outer layer are formed of the same wall-forming organic compounds, and the core is then surrounded by one layer coating.

In one embodiment, the outer layer does not contain any colorant. In another embodiment, the outer layer contains at least one colorant.

The term "wall-forming organic compound" refers to an organic compound or a combination of two or more different organic compounds as defined herein, which form a component of the layer(s) of the microcapsules. In a preferred embodiment, the 'wall-forming organic compound' contains at least one polymer.

In a particular embodiment, encapsulated colorant(s) may be present in the composition of the present invention in an amount in active matter of encapsulated pigments ranging from 0.5% to 20% by weight, in particular from 1% to 15% by weight, and more particularly from 2% to 12% by weight, relative to the total weight of the composition.

The microcapsules will be integrated in the cosmetic formula generally at the latest stages of the formulation and after filtering stages if any, to avoid the microcapsules being broken. Preferably, the microcapsules are added and mixed uniformly at temperatures under 50°C. They are mixed gently with a paddle rather than a homogenizer.

The microcapsules may have the ability of being more easily breakable in contact with aqueous phase, preferably in contact with hydrophilic agent(s) (e.g., water, polyols, glycols, alcohols). The microcapsules may advantageously swell in contact with such hydrophilic agent(s) as defined hereunder. The microcapsules are advantageously deformable when applied on a keratin material and consequently provide a soft feeling to the user. Furthermore, their small size contributes to not creating any discomfort or unfavourable feeling when applied.

However, the microcapsules are soft enough to rupture upon very slight rubbing or pressing of the skin in order to release their content but, nevertheless, are durable enough to avoid destruction of the coating during manufacture and storage of the corresponding composition.

In addition, the microcapsule allows the use of regular equipment for the preparation of the compositions of the present invention because substantially no coloring of the apparatus occurs during the manufacturing process.

Accordingly, the microcapsules are of particular interest since they can mask the original color of the encapsulated colorants, increase the stability of these colorants against degradation, and prevent undesirable release of the encapsulated colorants into the composition during the manufacturing process and prolonged storage.

The composition may contain at least from 0.1% to 20% by weight, preferably from 0.5% to 15% by weight and more preferably from 2% to 10 % by weight of microcapsules relative to the total weight of the composition.

A preferable constitution of the microcapsules will be described in detail below.

1-4-1. First embodiment of a microcapsule containing releasable colorant(s)

In a first embodiment, generally, the microcapsules have average particle sizes of less than 800 μm, more preferably less than about 400 μm, advantageously from 1 μm to 300 μm, in particular from 5 μm to 200 μm, and more particularly from 10 μm to 100 μm in diameter.

The microcapsules containing releasable colorant(s) are multilayered microcapsules. The microcapsules contain:

- a core, preferably uncolored core, containing, preferably consisting of, one organic material, and
- at least one layered coating surrounding the core, the layered coating containing at least one polymer, and at least one colorant. Advantageously it contains at least one binder.

Preferably, the microcapsule contains at least two layers, preferably at least one organic colored inner layer and one organic outer layer of different color from that of the organic colored inner layer.

Preferably, the core contains at least one monosaccharide or its derivatives as the organic material, in particular a monosaccharide-polyol advantageously selected from the group consisting of mannitol, erythritol, xylitol, sorbitol and mixtures thereof, preferably mannitol.

Advantageously, the layered coating surrounding the core contains at least one hydrophilic polymer(s) selected from the group consisting of polysaccharides and derivatives thereof, preferably the ones including one type of ose or several type of ose(s), preferably several type of ose(s) including at least D-glucose units, in particular starch and derivatives, cellulose or its derivatives, and more preferably starch and derivatives.

Preferably, the microcapsule includes at least one lipid-based material, preferably with

amphiphilic properties such as lecithins and in particular hydrogenated lecithin.

Advantageously the core represents from 10% to 90% by weight, preferably 20% to 80% by weight, more preferably from 30% to 70% by weight, and still more preferably from 40% to 60% by weight, relative to the total weight of the microcapsule.

Advantageously, the colorant(s) represent from 20% to 90%, preferably from 30% to 80%, and in particular from 50% to 75% by weight relative to the microcapsule.

Particularly the microcapsule contains at least:
- an inner core made of monosaccharide-polyol, preferably mannitol,
- at least two layers of different color from each other,
- at least one hydrophilic polymer preferably selected from polysaccharide or its derivatives, and more preferably from starch or derivatives, and advantageously at least one lipid based material, preferably an amphiphilic compound, and more preferably a phospholipid, even more preferably phosphoacylglycerol such as hydrogenated lecithin.

In one embodiment, each layer from the microcapsule contains at least one specific colorant or a specific blend of colorant(s). In one embodiment, the outer layer from the microcapsule contains at least one specific colorant or a specific blend of colorant(s). Particularly the colorants are pigments, preferably selected from the group consisting of metallic oxides. In one embodiment, one layer from the microcapsule contains iron oxides and titanium dioxide (TiO_2) as colorants. In one embodiment, one layer from the microcapsule only contains TiO_2 as a colorant.

The composition of the present invention may further contain from 0.1% to 70% by weight relative to the weight of the composition, of additional cosmetic ingredient(s) selected from volatile and non-volatile silicon or hydrocarbon oils, surfactants, fillers, additional gelifying agents, thickening agents, film forming agents, polymers, preservatives, silicone elastomers, self-tanning agents, additional non-entrapped colorants, cosmetic actives, pH regulators, perfumes, UV filters and mixtures thereof.

1-4-1-1. Core

In a first embodiment of the invention, the core is made of at least an organic material. The size of the core preferably ranges from 500 nm to 150 μm in diameter. Preferably the core is in a solid and/or crystal form at room temperature under atmospheric pressure. In a particular embodiment, the organic material may have high water dissolvability.

Preferably, the core is water-soluble or water dispersible.

In a particular embodiment, the core is uncolored, *i.e.,* it does not contain colorant material.

In a particular embodiment, the core consists of only one compound. This compound is

organic and more preferably is a natural compound.

In a preferred embodiment, the core is sugar-alcohol, preferably a monosaccharide-polyol advantageously selected from mannitol, erythritol, xylitol, sorbitol. In a particular embodiment, the core is made of mannitol and more preferably exclusively made of mannitol. In an alternative embodiment, the core contains at least mannitol and at least one additional ingredient being preferably a polymer selected from hydrophilic polymers. In particular, such a core may contain mannitol and hydrophilic polymers chosen among cellulose polymers, starch polymers and their mixture, preferably their mixture. In a preferred embodiment, the cellulose polymer is a carboxymethylcellulose and the starch polymer is a non-modified natural starch, for example corn starch.

The core may be constituted by a seed (or crystal) of one of the previous materials.

The core is preferably contained in an amount of from 1% to 50% by weight, preferably from 4% to 40% by weight, in particular from 5% to 30% by weight, and more particularly from 10% to 20% by weight with respect to the total weight of the microcapsule.

The mannitol is preferably contained in an amount of from 2% to 100% by weight, preferably from 5% to 100% by weight, and in particular 100% by weight with respect to the total weight of the core.

The mannitol is preferably contained in an amount of from 1% to 50% by weight, preferably 4% to 40% by weight, in particular from 5% to 30% by weight, and in particular from 10% to 20% by weight with respect to the total weight of the microcapsule.

1-4-1-2. External Layer(s)

As disclosed previously, the core is advantageously surrounded with external layer(s) preferably containing at least one inner layer and one outer layer. In the first embodiment, these layers preferably extend concentrically with respect to the core. The layer(s) is/are preferably organic, i.e., contain(s) at least one organic compound as wall-forming material. Preferably, the inner and/or outer layer(s) include(s) at least one polymer, and in particular a hydrophilic polymer.

(a) Polymer(s)

In the first embodiment, the microcapsules, and in particular the external layer(s) contain(s) hydrophilic polymers selected from the group consisting of polysaccharides and derivatives, acrylic or methacrylic acid homopolymers or copolymers or salts and esters thereof, and their mixture.

In a preferred embodiment, the microcapsule, and in particular the external layer(s), contain(s) hydrophilic polymers selected from the group consisting of polysaccharides and derivatives, and in particular starch polymers.

The polymer(s) is (are) advantageously selected from (poly)(alkyl)(meth)acrylic acid and their derivatives, notably (poly)(alkyl)(meth)acrylate and their derivatives, preferably from alkylacrylic /alkylmethacrylic acid copolymers and their derivatives, and most preferably is a copolymer of ethyl acrylate, methyl methacrylate and low content of methacrylic acid ester with quaternary ammonium groups provided under the trade name of EUDRAGIT RSPO from Evonik Degussa.

The polysaccharides and derivatives are preferably selected from the group consisting of chitosan polymers, chitin polymers, cellulose polymers, starch polymers, galactomannans, alginates, carrageenans, mucopolysaccharides, and their derivatives, and mixtures thereof.

In a preferred embodiment, the external layer(s) is/are devoid of microcrystalline cellulose.

In a particularly preferred embodiment, the polysaccharides and their derivatives are preferably selected from those including one type of ose or several types of ose(s), preferably several types of oses, in particular at least D-Glucose unit(s) as ose(s), preferably starch polymers, cellulose polymers, and derivatives, and mixtures thereof.

In a preferred embodiment, the microcapsule contains at least one hydrophilic polymer selected from the group consisting of starch and its derivatives, in particular corn starch, cellulose and its derivatives, homo- and/or co-polymer of methacrylic acid and/or methacrylic acid ester or co-polymer of (alkyl)acrylic acid and/or (alkyl)methacrylic acid and their derivatives, preferably their salts and their esters, and in particular the capsule contains polymethyl methacrylate.

In a preferred embodiment, the microcapsule contains at least one hydrophilic polymer selected from the group consisting of starch and its derivatives, in particular corn starch.

Starch usable according to the present invention is usually issued from vegetable raw materials, such as rice, soybeans, potatoes, or corn. Starch can be unmodified or (by analogy with cellulose) modified starch. In a preferred embodiment, the starch is unmodified.

Preferred homo- and /or co-polymers of methacrylic acid and/or methacrylic acid ester are those wherein the copolymer of methyl methacrylate and ethyl acrylate has a molecular weight from 750 to 850 kDa.

Cellulose derivatives include, for example, alkali celluloses carboxymethyl cellulose (CMC), cellulose esters and ethers, and aminocelluloses. In a particular embodiment, the cellulose is a carboxymethyl cellulose (CMC).

In a preferred embodiment, the capsule contains at least starch derivative, in particular corn starch, polymethyl methacrylate, a co-polymer of (alkyl)acrylic acid and/or (alkyl)methacrylic acid and their derivatives preferably their salts and their esters, and/or cellulose derivatives.

Preferably, the microcapsule contains polymer(s) which are not cross-linked. The polymer(s) may be in one or several layer(s). In another embodiment, the polymer(s) may be in the core. The microcapsule may contain polymer(s) in the core and/or in the layer(s). In a particular embodiment, the polymer(s) is (are) in the core and in the layer(s). In an embodiment, the core contains at least starch and/or cellulose derivative as polymer(s). When the starch is contained within the core, it represents the main ingredient of such a core, i.e., the weight amount of starch is greater than the respective amount of other compounds of the core. The polymer may represent from 0.5% to 20% by weight of the microcapsule, in particular from 1% to 10% by weight, and preferably from 2% to 8% by weight of the microcapsule.

The different layers forming the coating may be based on identical or different polymers. Advantageously, they will be formed from the same polymer. In contrast, the layers will be advantageously differently colored. This different colors may be obtained through the use of different colorants but also the use of different concentrations in at least one colorant when the colorant will be the same for two layers.

In a particular embodiment, the outer layer contains at least one colorant. In another embodiment, the outer layer does not contain any colorant.

(b) Colorant(s)

In the first embodiment, the microcapsules, and in particular the external layer(s) contain(s) colorant(s).

The term "colorant" includes any organic or inorganic pigment or colorant approved for use in cosmetics by the CTFA and the FDA for use in cosmetic formulations. Thus the term "colorant" refers to organic pigments such as synthetic or natural dyes selected from any of the well-known FD&C or D&C dyes, to inorganic pigments such as metal oxides, or lakes such as the ones based on cochineal carmine, barium, strontium, calcium or aluminum and any combination (blend) thereof. Such colorants are detailed hereinafter. In a particular embodiment, the colorant may be water-soluble or water-dispersible. In another embodiment, the colorant useful according to the present invention may be oil-soluble or oil-dispersible or with limited solubility in water. In a preferred embodiment, the colorant is an inorganic pigment, more preferably a metal oxide. Advantageously, the colorants of the multilayered microcapsules are primary metal oxides selected from iron oxides, titanium dioxide, aluminum oxide, zirconium oxides, cobalt oxides, cerium oxides, nickel oxides, tin oxide or zinc oxide, or composite oxides, more preferably an iron oxide selected from red iron oxide, yellow iron oxide or black iron oxide, or a mixture thereof.

The layer(s) may also contain lakes corresponding to an organic colorant secured to a substrate. Such (a) lake(s) is (are) advantageously chosen among the following material, and their mixture(s):

- carmin of cochineal;
- organic pigments of azoic, anthraquinonic, indigoid, xanthenic, pyrenic, quinolinic,

triphenylmethane, fluoran colorants; among the organic pigments may be cited those known under the following trademark references: D&C Blue No. 4, D&C Brown No. 1, D&C Green No. 5, D&C Green No. 6, D&C Orange No. 4, D&C Orange No. 5, D&C Orange No. 10, D&C Orange No. 11, D&C Red No. 6, D&C Red No. 7, D&C Red No. 17, D&C Red No. 21, D&C Red No. 22, D&C Red No. 27, D&C Red No. 28, D&C Red No. 30, D&C Red No. 31, D&C Red No. 33, D&C Red No. 34, D&C Red No. 36, D&C Violet No. 2, D&C Yellow No. 7, D&C Yellow No. 8, D&C Yellow No. 10, D&C Yellow No. 11, FD&C Blue No. 1, FD&C Green No. 3, FD&C Red No. 40, FD&C Yellow No. 5, and FD&C Yellow No. 6;
- the water-insoluble salts of sodium, potassium, calcium, barium, aluminum, zirconium, strontium, titanium, of acid colorants such as azoic, anthraquinonic, indigoids, xanthenic, pyrenic, quinolinic, triphenylmethane, and fluoran colorants, these colorants may include at least one carboxylic or sulfonic acid group.

The organic lakes may also be protected by an organic support such as rosin or aluminum benzoate.

Among the organic lakes, we may in particular cite those known under the following names: D&C Red No. 2 Aluminum lake, D&C Red No. 3 Aluminum lake, D&C Red No. 4 Aluminum lake, D&C Red No. 6 Aluminum lake, D&C Red No. 6 Barium lake, D&C Red No. 6 Barium/Strontium lake, D&C Red No. 6 Strontium lake, D&C Red No. 6 Potassium lake, D&C Red No. 6 Sodium lake, D&C Red No. 7 Aluminum lake, D&C Red No. 7 Barium lake, D&C Red No. 7 Calcium lake, D&C Red No. 7 Calcium/Strontium lake, D&C Red No. 7 Zirconium lake, D&C Red No. 8 Sodium lake, D&C Red No. 9 Aluminum lake, D&C Red No. 9 Barium lake, D&C Red No. 9 Barium/Strontium lake, D&C Red No. 9 Zirconium lake, D&C Red No. 10 Sodium lake, D&C Red No. 19 Aluminum lake, 20 D&C Red No. 19 Barium lake, D&C Red No. 19 Zirconium lake, D&C Red No. 21 Aluminum lake, D&C Red No. 21 Zirconium lake, D&C Red No. 22 Aluminum lake, D&C Red No. 27 Aluminum lake, D&C Red No. 27 Aluminum/Titanium/Zirconium lake, D&C Red No. 27 Barium lake, D&C Red No. 27 Calcium lake, D&C Red No. 27 Zirconium lake, D&C Red No. 28 Aluminum lake, D&C Red No. 28 Sodium lake, D&C Red No. 30 lake, 25 D&C Red No. 31 Calcium lake, D&C Red No. 33 Aluminum lake, D&C Red No. 34 Calcium lake, D&C Red No. 36 lake, D&C Red No. 40 Aluminum lake, D&C Blue No. 1 Aluminum lake, D&C Green No. 3 Aluminum lake, D&C Orange No. 4 Aluminum lake, D&C Orange No. 5 Aluminum lake, D&C Orange No. 5 Zirconium lake, D&C Orange No. 10 Aluminum lake, D&C Orange No. 17 Barium lake, D&C Yellow No. 5 Aluminum lake, D&C Yellow No. 5 Zirconium lake, D&C Yellow No. 6 Aluminum lake, D&C Yellow No. 7 Zirconium lake, D&C Yellow No. 10 Aluminum lake, FD&C Blue No. 1 Aluminum lake, FD&C Red No. 4 Aluminum lake, FD&C Red No. 40 Aluminum lake, FD&C Yellow No. 5 Aluminum lake, and FD&C Yellow No. 6 Aluminum lake.

The chemical material corresponding to each of these organic colorants previously cited are mentioned in the book called <International Cosmetic Ingredient Dictionary and Handbook>, Edition 1997, pages 371 to 386 and 524 to 528, published by <The Cosmetic, Toiletry, and Fragrance Association>, of which the content is hereby incorporated by reference into the

present specification.

In a preferred embodiment, the lake(s) is/are selected from carmin of cochineal and the water-insoluble salts of sodium, potassium, calcium, barium, aluminum, zirconium, strontium, titanium, of acid colorants such as azoic, anthraquinonic, indigoid, xanthenic, pyrenic, quinolinic, triphenylmethane, and fluoran colorants, given that these colorants may include at least one carboxylic or sulfonic acid group, and their mixture.

In a preferred embodiment, the lake(s) is/are selected from carmin of cochineal and the water-insoluble salts of sodium, calcium, aluminum, and their mixture.

As lake incorporating carmine we may cite the commercial references:
CARMIN COVALAC W 3508, CLOISONNE RED 424C et CHROMA-LITE MAGENTA CL4505.

The water-insoluble aluminum salts are preferably selected from FDC Yellow No. 5 Aluminum lake, FDC Blue No. 1 Aluminum lake, FDC Red No.40 Aluminum lake, FDC Red No. 30 Aluminum lake, FDC Green No. 5 Aluminum lake, and their mixtures. As compounds incorporating such inorganic lakes may notably be cited the commercial references: INTENZA FIREFLY C91-1211, INTENZA AZURE ALLURE C91-1251, INTENZA THINK PINK C91-1236.

The water-insoluble calcium salts are preferably selected from Red No. 7 Calcium lake. As compounds incorporating such inorganic lakes may notably be cited the commercial references: INTENZA MAGENTITUDE C91-1234, INTENZA HAUTE PINK C91-1232, INTENZA RAZZLED ROSE C91-1231, INTENZA AMETHYST FORCE C91-7231, INTENZA PLUSH PLUM C91-7441, INTENZA ELECTRIC CORAL 30 C91-1233, FLORASOMES-JOJOBA-SMS-10% CELLINI RED-NATURAL and their mixture.

The water-insoluble sodium salts are preferably selected from Red No. 6 Sodium lake and Red No. 28 Sodium lake, and their mixture. As compounds incorporating such inorganic lakes may notably be cited the commercial references: INTENZA MANGO TANGO C91-1221 and INTENZA NITRO PINK C91-1235.

In an embodiment, the colorants present in the microcapsules are selected from the group consisting of inorganic pigments, organic pigments and their mixture, preferably is at least one inorganic pigment, more preferably at least a mixture of inorganic pigments, even more preferably selected from metallic oxides, and in particular from iron oxide(s), titanium dioxide particles and their mixture, preferably their mixture.

The composition of the present invention may contain a mixture of two or more colorants, either encapsulated individually in microcapsules and/or one or more blends of colorants encapsulated within the multilayered microcapsules. In this specific embodiment, each layer of the

microcapsule may contain at least one specific colorant or a specific blend of colorant(s). In this specific embodiment, the composition of the present invention contains two or more microcapsules having different colors.

A person skilled in the art knows how to choose colorants and combinations of colorants to produce a desired color effect or color change. As stated hereinbefore, the microcapsules contain preferably at least titanium dioxide and/or iron oxides in their coating, preferably at least titanium dioxide. In a preferred embodiment, the microcapsules contain at least titanium dioxide and iron oxides in their coating. In a specific embodiment, the outer layer of the microcapsules contains titanium dioxide, more preferably as the sole colorant.

In a specific embodiment, the outer layer of the microcapsules contains organic pigments or iron oxides.

The colorants are present in an amount ranging from 20% to 90% by weight, preferably from 30% to 80% by weight, and more preferably from 50% to 75% by weight relative to the total weight of the microcapsule.

In a particular embodiment, the microcapsules contain a metallic oxide selected from the group consisting of iron oxides, and titanium oxides, present in an amount ranging from 20% to 90% by weight, preferably from 30% to 85% by weight, and more preferably from 50% to 85% by weight, relative to the total weight of the microcapsule.

In particular the titanium oxide may be present from 28% to 80% by weight, preferably from 30% to 75% by weight, and more preferably from 30 to 50% by weight, relative to the total weight of the microcapsule. In a particular embodiment, the titanium oxide may be present from 50% to 80% by weight, in particular from 55% to 70% by weight, and more particularly from 55% to 65% by weight, relative to the total weight of the microcapsule.

In particular the iron oxides may be present from 5% to 75% by weight, preferably from 8% to 65% by weight relative to the total weight of the microcapsule. In a particular embodiment, the iron oxides may be present in an amount higher than 15% by weight, preferably higher than 30% by weight, and in particular from 40% to 65% by weight, relative to the total weight of the microcapsule.

In a preferred embodiment, in at least one layer, and preferably in every layer, the colorants are the main ingredients, i.e., represent at least 40% by weight of the layer(s), preferably at least 75% by weight of the layer(s), more preferably at least 95% by weight of the total weight of the layer(s).

In a preferred embodiment, the mean thickness of the titanium dioxide layer ranges from 5 μm to 150 μm.

(c) Binder or Lipid-Based Material

The inner and/or outer layer(s) may also include advantageously at least one binder, preferably a lipid-based material. In a particular embodiment of this invention, such a lipid-based material may have amphiphilic properties, that is to say having an apolar part and a polar part.

Such a lipid-based material can include at least one or several C_{12}-C_{22} fatty acid chain(s) such as those selected from stearic acid, palmitic acid, oleic acid, linoleic acid, linolenic acid, etc., and mixtures thereof. Preferably these fatty acids chains are hydrogenated. Eventually, these fatty acid chains may be the apolar part of a lipid-based material.

Such a lipid-based material is preferably selected from phospholipids. These phospholipids are preferably selected from phosphoacylglycerol, more preferably selected from lecithins, and are in particular hydrogenated lecithin.

The lipid-based material may represent from 0.05% to 5% by weight of the microcapsule, in particular from 0.1% to 1% by weight of the microcapsule.

By combining three or more compounds (e.g., sugar alcohols, polymers, lipid-based materials) in the microcapsule of different hardness and/or water solubility, it is possible to adjust the time required for colorant-encapsulated microcapsules to break down on the skin so that, by varying the method or intensity of application onto the skin, it is possible to adjust the preferred coloration or gradation pattern.

Thus, in a preferred embodiment, the multi-layer coating contains at least starch as a polymer and at least one lipid-based material, which is preferably lecithin.

In an advantageous embodiment the microcapsules include at least one monosaccharide or its derivatives and at least one polysaccharide or its derivatives.

In a preferred embodiment, the microcapsules include a core containing a monosaccharide derivative and a coating containing a polysaccharide (or its derivatives) including one type of ose or several types of ose(s), preferably several types of oses.

In a more preferred embodiment, the microcapsules include a core containing a monosaccharide polyol, preferably selected from mannitol, erythritol, xylitol, sorbitol, and a coating containing a polysaccharide (or its derivatives) including as ose(s) at least one or more D-Glucose unit(s).

In a preferred embodiment, the microcapsules include three or more colorants in different layers.

In a preferred embodiment, the microcapsules additionally include a binder, for example, a lipid-based material chosen from phospholipids, advantageously selected from phosphoacylglycerol and in particular from lecithins.

In a particular embodiment, the microcapsules contain mannitol, starch polymer and a lipid-based material.

Referring to figure 1, in a preferred embodiment, the present invention advantageously provides a color-changing microcapsule containing:
i) a core (A), preferably having a size of less than 800 μm, more preferably less than about 400 μm, advantageously from 1 μm to 300 μm, in particular from 5 μm to 200 μm, and more particularly from 10 μm to 100 μm in diameter, which preferably does not contain any colorant, and containing at least one organic core preferably selected from at least one sugar alcohol preferably a monosaccharide-polyol advantageously selected from the group consisting of mannitol, erythritol, xylitol, and sorbitol;
ii) one first layer (B) surrounding the core containing:
- at least one colorant, preferably iron oxide(s), and
- a binder selected from the group consisting of a polymer and a lipid-based material, preferably their mixture;
iii) one second layer (C) surrounding the first layer (B), preferably having a thickness of 5 μm to 500 μm, containing:
- titanium dioxide particles, and
- a binder selected from the group consisting of a polymer and a lipid-based material, preferably their mixture;
iv) optionally one third layer (D) surrounding the second layer (C) containing:
- at least one colorant, and
- a binder selected from the group consisting of a polymer and a lipid-based material, preferably their mixture;
v) optionally one fourth layer (E) surrounding the third layer (D), if any, or surrounding the second layer (C) containing:
- at least one wall-forming polymer preferably selected from polysaccharides such as cellulose derivatives, in particular cellulose ether and cellulose ester, from (poly)(alkyl)(meth)acrylic acid and its derivatives, notably (poly)(alkyl)(meth)acrylate and its derivatives, and preferably from alkylacrylic /alkylmethacrylic acid copolymers and their derivatives.

In a preferred embodiment, the polymer is a hydrophilic polymer selected from the group consisting of starch and its derivatives, in particular corn starch.

As examples of commercially available microcapsules used in the composition of the present invention, we may refer to the following microcapsules produced by Korea Particle Technology KPT under the commercial names:
- Magic50-BW0105 from KPT: ash gray spherical microcapsule containing mannitol, iron oxide red, iron oxide yellow, iron oxide black, hydrogenated lecithin, titanium dioxide, zea mays (corn) starch, having a 60-200 Mesh particle size.

1-4-2. Second embodiment of microcapsule containing releasable colorant(s)

In the second embodiment, the microcapsule contains:
- a core including at least one colored core and eventually at least one inner color layer(s), and
- a shell having at least one pressure-breakable wall layer surrounding the core, an optional outer color layer and an optional outmost shell.

In a preferred embodiment, the microcapsule contains colorant(s) selected from inorganic pigment(s), preferably selected from metal oxides, such as iron oxides and titanium oxide.

Preferably the colored core includes at least one inorganic pigment advantageously selected from at least one metallic oxide, more advantageously selected from at least one iron oxide.

Preferably the pressure-breakable wall layer includes at least one inorganic pigment advantageously selected from at least one metallic oxide, more advantageously selected from at least one titanium oxide.

Preferably such iron oxides are located at least in the colored core and the titanium oxides are located at least in a pressure-breakable wall layer surrounding the core.

The microcapsules contain at least 70% by weight of colorant(s), preferably of inorganic pigment(s), preferably of a mixture of inorganic pigments, preferably of metallic oxides such as iron oxides and titanium oxides, compared to the total weight of the microcapsules.

Generally average particle size diameters of colorant microcapsules up to about 800 microns are used according to the present invention. Preferably the average particle size diameter of the colorant microcapsules is less than about 400 microns for skin care applications. Advantageously the average particle size diameter is in the range of about 10 to 350 microns. Preferably, the average particle size will be from 50 μm to 800 μm, and in particular from 60 μm to 400μm.

Advantageously the microcapsule has a mean particle size of about from 18 to 270 mesh (around from 1000 μm to 53 μm), particularly about from 25 to 170 mesh (around from 710 μm to 90 μm).

In particular for a skincare composition of the present invention, the amount of microcapsules will range from 0.1% to 5%, preferably from 0.2% to 3% by weight relative to the total weight of composition.

In particular for a makeup composition of the present invention, the amount of microcapsules will range from 0.5% to 20%, preferably from 1% to 15%, more preferably from 2% to 10% by weight relative to the total weight of composition.

In a particular embodiment, the encapsulated colorant(s) may be present in a composition of the present invention in an amount in active matter of encapsulated pigments ranging from 0.5% to

20% by weight, in particular from 1% to 15% by weight, and more particularly from 2% to 12% by weight, relative to the total weight of the composition.

They will be integrated in the cosmetic formula generally at the latest stages of the formulation and after filtering stages if any, to avoid broken. Preferably, the microcapsules of the present invention are added and mixed uniformly at temperatures under 50°C. They are mixed gently with a paddle rather than a homogenizer.

In a particular aspect of the present invention, more than 60%, preferably more than 70%, particularly more than 80%, and more particularly more than 90% of microcapsules will be ruptured to release the inner colorant within 1 minute, preferably from 1 to 40 seconds, particularly from 1 to 30 seconds, and more particularly from 1 to 20 seconds after pressing, rubbing, wiping and/or scrubbing with the hands or an implement. However, the ratio and time-limit is not critical in the present invention.

1-4-2-1. Core (colorant and binder or lipid-based material)

In the second embodiment, the core of the microcapsule contains a colored core which contains at least one colorant and advantageously at least one binder, for example a lipid-based material.

The colorant(s) are not limited specifically, and the species described above are preferably used.

The binder is preferably selected from at least one hydrophilic polymer, at least one lipid-based material, and their mixture, preferably their mixture. In general, it is difficult to form a coating layer by using only colorant components or particles without using any binder. Further, even if a coating layer without a binder is formed with difficulty, such a coating layer may be easily damaged or ruptured or any of the components or particles may be easily removed from the coating layer. Therefore, a binder may be employed in order to promote the coating process and to improve the durability of the coating layer. Such a binder is selected from adhesive polymeric materials, which can act as wall-forming materials (wall-forming polymeric materials).

In the present invention, the binder is preferably selected from at least one wall-forming material, from a lipid-base material, and their mixture. More preferably, the binder is a mixture which contains both a polymer as a wall-forming material and a lipid-base material as a coating base.

The coating base refers to a hydrophilic coating base, a hydrophobic coating base, or a lipid-based coating base. Since the hydrophilic coating base may be extracted together with colorant and the hydrophobic coating base may give a feeling of the presence of foreign substances due to its too strong film property, it is preferable to employ a lipid-based coating base.

In a particular embodiment, such a lipid-based material may have amphiphilic properties, that is

to say having an apolar part and a polar part.

Such a lipid-based material can include at least one or several C_{12}-C_{22} fatty acids chain such as selected from stearic acid, palmitic acid, oleic acid, linoleic acid, linolenic acid, etc. and mixtures thereof. Preferably these fatty acids chains are hydrogenated. Eventually, these fatty acid chains may be the apolar part of a lipid-based material.

Lipid-based materials are amphiphilic materials having both a polar part and an apolar part in one molecule and include, for example, a C_{12}-C_{22} fatty acid chain selected from the group consisting of stearic acid, palmitic acid, oleic acid, linoleic acid, linolenoic acid, and mixtures thereof. The fatty acid chain may be hydrogenated, and optionally forms the apolar portion of the lipid-based materials.

The lipid-based materials can be selected form the group consisting of a phospolipid such as phosphatidylcholine, phosphatidylethanolamine, phosphatidic acid or phosphatidylserine, a sphingolipid such as sphingosine-1-phosphate or sphingomyelin and ceramide, preferably ceramide or lecithin which is a phospholipid mixture, particularly hydrogenated lecithin.

The amount of lipid-based materials can be determined by considering the type and amount of wall-forming polymers as well as other components such as colorants and/or titanium dioxide particles. In general, however, the amount of lipid-based materials can be selected, in terms of the total weight of each layer, from 0.1% to 30 % by weight, particularly from 0.2% to 25% by weight, preferably from 0.3% to 20% by weight and more preferably from 0.4% to 20% by weight. When the amount of lipid-based materials is less than 0.1% by weight, the breakability or dissolution ability may be decreased, and when it is more than 25% by weight, the durability may be decreased or the stability during processing and storage may be decreased.

In the present invention, the wall-forming polymer is selected from hydrophilic polymers. The term "hydrophilic polymers" means a polymer which can form hydrogen bond with water or alcohol compounds (especially selected from lower alcohols, glycol and polyol), particularly those having O-H, N-H and S-H bonds in the molecule.

The hydrophilic polymer can be selected from the following polymers or a mixture thereof:
- acrylic or methacrylic acid homopolymers or copolymers or salts and esters thereof and in particular the products sold under the names Versicol F or Versicol K by the company Allied Colloid, Ultrahold 8 by the company Ciba-Geigy, and polyacrylic acids of Synthalen K type, and salts, especially sodium salts, of polyacrylic acids (corresponding to the INCI name sodium acrylate copolymer) and more particularly a crosslinked sodium polyacrylate (corresponding to the INCI name sodium acrylate copolymer (and) caprylic/capric triglycerides) sold under the name Luvigel EM by the company BASF;
- copolymers of acrylic acid and of acrylamide sold in the form of the sodium salt thereof under the names Reten by the company Hercules, sodium polymethacrylate sold under the name Darvan No. 7 by the company Vanderbilt, and the sodium salts of polyhydroxycarboxylic acids

sold under the name Hydagen F by the company Henkel;
- polyacrylic acid/alkyl acrylate copolymers, preferably modified or unmodified carboxyvinyl polymers; the copolymers most particularly preferred are acrylate/C_{10}-C_{30}-alkylacrylate copolymers (INCI name: Acrylates/C_{10-30} Alkylacrylate Cross polymer) such as the products sold by the company Lubrizol under the tradenames Pemulen TR1, Pemulen TR2, Carbopol 1382 and Carbopol ETD2020, Carbopol Ultrez 21, and even more preferentially Pemulen TR-2;
- alkylacrylic /alkylmethacrylic acid copolymers and their derivatives notably their salts and their esters, such as the copolymer of ethyl acrylate, methyl methacrylate and low amount of methacrylic acid ester with quaternary ammonium groups provided under the tradename of EUDRAGIT RSPO from Evonik Degussa;
- AMPS (polyacrylamidomethylpropanesulfonic acid partially neutralized with aqueous ammonia and highly crosslinked) sold by the company Clariant;
- AMPS/acrylamide copolymers such as the products Sepigel or Simulgel sold by the company SEPPIC, especially a copolymer of INCI name Polyacrylamide (and) C_{13}-C_{14} Isoparaffin (and) Laureth-7;
- polyoxyethylenated AMPS/alkyl methacrylate copolymers (crosslinked or non-crosslinked) of the type such as Aristoflex HMS sold by the company Clariant;
- anionic, cationic, amphoteric or nonionic chitin or chitosan polymers;
- cellulose polymers and their derivatives, preferably other than alkylcellulose, chosen from hydroxyethylcellulose, hydroxypropylcellulose, hydroxymethylcellulose, ethylhydroxyethylcellulose and carboxymethylcellulose, and also quaternized cellulose derivatives; in a preferred embodiment, the cellulose polymer is a carboxymethylcellulose;
- starch polymers and their derivatives, eventually modified; in a preferred embodiment, the starch polymer is a natural starch;
- vinyl polymers, for instance polyvinylpyrrolidones, copolymers of methyl vinyl ether and of malic anhydride, the copolymer of vinyl acetate and of crotonic acid, copolymers of vinylpyrrolidone and of vinyl acetate; copolymers of vinylpyrrolidone and of caprolactam; polyvinyl alcohol;
- optionally modified polymers of natural origin, such as galactomannans and derivatives thereof, such as konjac gum, gellan gum, locust bean gum, fenugreek gum, karaya gum, gum tragacanth, gum arabic, acacia gum, guar gum, hydroxypropyl guar, hydroxypropyl guar modified with sodium methylcarboxylate groups (Jaguar XC97-1, Rhodia), hydroxypropyltrimethylammonium guar chloride, and xanthan derivatives;
- alginates and carrageenans;
- glycoaminoglycans, hyaluronic acid and derivatives thereof; and
- mucopolysaccharides such as hyaluronic acid and chondroitin sulfates, and mixtures thereof.

Preferably, the hydrophilic polymers of the present invention can be selected from the group consisting of polysaccharides and their derivatives, homo- and/or co-polymers of acrylic or methacrylic acid or salts and esters thereof, and their mixture.

The polysaccharides and their derivatives can be selected from chitosan polymers, chitin polymers, cellulose polymers, starch polymers, galactomannans, alginates, carrageenans,

mucopolysaccharides, and their derivatives, and a mixture thereof.

The polysaccharides and their derivatives are preferably selected from the group consisting of starch polymers.

Preferably, the hydrophilic polymers can be selected from the group consisting of corn starch, polymethyl methacrylate, cellulose or its derivatives such as carboxymethylcellulose (CMC), cellulose ester and ether and aminocellulose, and a mixture thereof.

Preferably, the hydrophilic polymers can be selected from the group consisting of corn starch, polymethyl methacrylate, their derivatives, and a mixture thereof.

Preferred homo- and /or co-polymers of methacrylic acid and/or methacrylic acid ester are those wherein the copolymer of methyl methacrylate and ethyl acrylate has a molecule weight from 750 kDa to 850 kDa.

The hydrophilic polymer(s) used as a wall-forming material in the present invention are not cross-linked.

The amount of polymers or wall-forming polymers can be determined by considering the type and amount of colorants, titanium dioxide particles and/or lipid-based materials. In general, however, the amount of polymers or wall-forming polymers in each layer can be selected, in terms of total weight of each layer, from 0.1% to 30% by weight, particularly from 0.2% to 25% by weight, preferably from 0.3% to 20% by weight and more preferably from 0.4% to 20% by weight. When the content of lipid-based materials is less than 0.1% by weight, the breakability or dissolution ability may be decreased, and when it is more than 25% by weight, the durability may be decreased or the stability during processing and storage may be decreased. Such hydrophilic polymers described in this part may be implemented both as a shell-forming polymer and as a binder.

The core can be prepared in a form of particles, a powder, granules, micro spheres, and microcapsules, for example, by spray drying or fluid bed processing of the solution containing at least one colorant, at least one polymer as a wall-forming material and at least one lipid-based material in a solvent.

The size of the colored core, and more generally of the core, is not particularly limited and may be suitably chosen according to the finally desired microcapsule. For example, the size of the colored core, and more generally of the core, may be larger than 20 μm or more, particularly 30 μm or more, preferably 40 μm or more, more preferably 50 μm or more, and smaller than 800 μm or less, particularly 700 μm or less, preferably 600 μm or less, more preferably 500 μm or less.

The radius of the core is larger than 50%, specifically larger than 60%, preferably larger than 70%

and more preferably larger than 80%, relative to the total radius of the microcapsule. For example, the ratio between the radius of the core and the thickness of the shell may be from 1:0.05 to 1:0.5.

Alternatively, the amount of the core may be more than 30% by weight, specifically more than 40% by weight, preferably more than 50% by weight and more preferably more than 60% by weight, relative to the total weight of the microcapsule. Therefore, the microcapsule has a large loading amount of colorant in a particle.

The core can have one or more inner color layer(s) surrounding the colored core. The inner color layer(s) may be every layer located between the colored core and the pressure-breakable wall layer.

The inner color layer(s) include, for example, a first inner color layer, second inner color layer and third inner color layer, etc., wherein the colorants and binders contained in each inner color layer are the same or different from each other. In a preferred embodiment, the colored core can contain one or two inner color layer(s), preferably one inner color layer.

When the core has a colored core and an inner color layer, the colored core can be formed by a granulation of a solution for the colored core containing at least one colorant and preferably at least one binder, an inner color layer can be formed by coating the colored core with a solution for the inner color layer containing at least one colorant and preferably at least one binder. The coating process can be performed by a fluidized bed coating process.

The thickness of the inner color layer is not particularly limited and may be suitably chosen according to the finally desired microcapsule. For example, the thickness of the colored core, and more generally of the core, may be larger than 20 μm or more, particularly 40 μm or more, preferably 60 μm or more, more preferably 80 μm or more, and smaller than 200 μm or less, particularly 160 μm or less, preferably 120 μm or less, more preferably 100 μm or less.

Alternatively, the amount of the inner color layer may be from 20% to 80% by weight, specifically from 30% to 70% by weight, and preferably from 40% to 60% by weight, relative to the total weight of core.

In a particular embodiment, the colored core does not contain a binder and is surrounded by an inner color layer containing a colorant and a binder, by which pigments contained in the core will be more easily dispersed when the microcapsule is ruptured.

In the colored core, a binder can be used in an amount where the colorant will not fall apart or separate from the layer during the coating process and/or after the removal of solvent, and generally can be used in an amount selected from 1% to 30% by weight, preferably from 2% to 25% by weight, particularly from 5% to 20% by weight, and more particularly from 5% to 15% by weight relative to the total weight of the colored core.

In a preferred embodiment, the colorant(s), and preferably the pigment(s), still more preferably the iron oxide(s), is (are) present in the core in an amount of at least 70% by weight, specifically at least 75% by weight, preferably at least 80% by weight, more preferably at least 85% by weight, such as from 80% to 99% by weight, relative to the total weight of the core.

In a preferred embodiment, the colorant(s), and preferably the pigment(s), more preferably the iron oxide(s), is (are) present in an amount of at least 30% by weight, specifically at least 35% by weight, preferably at least 40% by weight, such as from 40% to 60% by weight, relative to the total weight of the microcapsule.

The amount of iron oxide(s) particles in the microcapsule may be from 20% to 60% by weight, preferably from 25% to 55% by weight, more preferably from 30% to 50% by weight, relative to the total weight of the microcapsule. More preferably, the amount of iron oxide(s) particles in the microcapsule may be from 30% to 58% by weight, preferably from 35% to 55% by weight, and more preferably from 40% to 50% by weight, relative to the total weight of the microcapsule.

1-4-2-2. Pressure-breakable wall layer or titanium dioxide particle layer

The microcapsule has a pressure-breakable wall layer including at least one colorant. The colorant(s) is (are) preferably selected from inorganic pigments, more preferably from metallic oxides and still more preferably from titanium dioxide particles.

Preferably the colorant contained in the pressure-breakable wall layer is distinct from the colorant(s) contained in the colored core, for instance being both metallic oxides distinct from each other.

In a preferred embodiment, the titanium dioxide particles are discontinuously dispersed in the layer and linked to each other by a binder.

The term "pressure-breakable" or "pressure-friable" means that a rupture can be easily made by pressing, rubbing, wiping and/or scrubbing with the hands or an implement such as a cloth, sponge or paper.

A pressure-breakable titanium dioxide particle layer can contain particles of titanium dioxide and a binder, and the binder can contain a wall-forming material.

In the pressure-breakable wall layer of the present invention, it is believed that the titanium dioxide particles lodged in the wall-forming materials will break the pressure-breakable wall layer in an irreversible manner and facilitate or increase the disintegration or dissolution of the wall layer. Further, it is also predicted that the titanium dioxide particles perform an important role in terms of the strength, durability, the pressure-breakability, and the resulting feeling of the wall layer.

For example, the pressure-breakable wall layer can be formed by the following procedure:
(a) dissolve or disperse titanium dioxide particles and a binder in an appropriate solvent to give a solution containing titanium dioxide particles and a binder,
(b) coat particles having the inner color layer with the solution obtained in (a) above, and
(c) optionally dry the resulting particles obtained in (b) above.

The coating may be preformed by using a fluidized bed process, but other coating processes can be utilized, if necessary. As to the appropriate solvents which can be utilized in the above procedure, mention can be made of water or a low boiling solvent such as methylene chloride, methanol and ethanol.

The titanium dioxide particle layer, of which the thickness can vary depending on the amount of titanium dioxide used and/or the type of binder, may have a thickness of 10 μm or more, preferably 20 μm or more, more preferably 30 μm or more, particularly 40 μm or more, commonly 300 μm or less, preferably 250 μm or less, more preferably 200 μm or less, and particularly 150 μm or less.

The amount of titanium dioxide particles in the pressure-breakable wall layer is preferably selected from 50% to 99% by weight, more preferably from 60% to 98% by weight, even more preferably from 70% to 97% by weight, and particularly from 80% to 95% by weight, in terms of total weight of the pressure-breakable wall layer. Preferably the amount of colorant(s), and in particular of titanium dioxide particles, represent less than 100% of the pressure-breakable wall layer.

The amount of titanium dioxide particles in the microcapsule is preferably selected from 20% to 60% by weight, preferably from 25% to 55% by weight, and more preferably from 30% to 50% by weight, relative to the total weight of the microcapsule.

The colorant(s) in the colored core, preferably iron oxide(s), and the colorant(s) in the pressure-breakable wall layer, preferably titanium dioxide particles, are both present in a respective total amount in the microcapsules such as the weight ratio of the colorant(s) in the colored core, and preferably iron oxide(s), relative to colorant(s) in the pressure-breakable wall layer, preferably titanium dioxide particles, is greater than or equal to 1.

The iron oxide(s) and the titanium dioxide particles are both present in a respective total amount in the microcapsules such as the weight ratio of the iron oxide(s) relative to the titanium dioxide particles is greater than or equal to 1.

The mean diameter or size of the titanium dioxide particles is not specifically limited but has a mean diameter of usually from 10 nm to 20 μm, preferably from 50 nm to 10 μm, more preferably from 100 nm to 5 μm, and particularly from 150 nm to 5 μm. A mean diameter or size of less than 10 nm of titanium dioxide particles may result in a decrease in the

pressure-breakable ability, and a mean diameter of more than 20 μm may make the formation of the titanium dioxide particle layer difficult. Titanium dioxide particles having a first particle size of less than the above range but having a second particle size falling within the above particle size range can be applicable in the present invention.

1-4-2-3. Optional outer color layer

The microcapsule additionally contains an optional outer color layer on the pressure-breakable titanium dioxide particle layer. The outer color layer can be formed by coating the titanium dioxide particle layer with a solution having a colorant and a binder, for example, by a fluidized bed process. The colorant and binder used in the outer color layer can be the same or different from those used in the inner color layer.

In general, the outer color layer is provided so as to impart a visual color different from the white color produced by the titanium dioxide particle layer and/or the color of the inner color layer. Therefore, a colorant in the outer color layer can be used in an amount that does not disturb the color developed by the inner color layer when the microcapsules are scrubbed.

The amount of the outer color layer can be from 1% to 60% by weight, preferably from 2% to 50% by weight, more preferably from 3% to 40% by weight, and particularly from 4% to 30% by weight relative to the total weight of core. However, the amount of the colorant in the outer color layer may be from 0.01% to 5% by weight, preferably from 0.05% to 4.5% by weight, more preferably from 0.1% to 4% by weight, and particularly from 0.5% to 3.5% by weight relative to the total weight of the colorant in the inner color layer.

The amount of colorant in the outer color layer may be additionally increased if the color of the outer color layer would not disturb the color of the inner color layer. A person skilled in the art can choose the color and amount of colorant in the outer color layer in an appropriate manner by considering the color and amount of colorants contained in the inner color layers and the desired color to be finally developed.

The thickness of the outer color layer is not particularly limited and may be suitably chosen according to the finally desired microcapsule. For example, the outer color layer may have a thickness which is larger than 20 μm, particularly 40 μm, preferably 60 μm, and more preferably 80 μm, and which is smaller than 200 μm, particularly 150 μm, preferably 120 μm, and more preferably 100 μm.

1-4-2-4. Outmost shell

The microcapsule can contain a protective outmost shell on a pressure-breakable titanium dioxide particle layer or an additional outer color layer to protect the microcapsule against moisture in the air during storage or to ensure long-term stability of the microcapsule in a carrier, notably in a solution.

The outmost shell can be made from at least one polymer, and preferably can be made from at

least one polymer selected from the group consisting of polysaccharides and their derivatives, acrylic or methacrylic acid homopolymers or copolymers or salts and esters thereof, polystyrene-maleic anhydride copolymers, and their mixtures, such as poly(meth)acrylate, cellulose ether, cellulose ester and their derivatives, and their mixtures.

The amount of the outmost shell is selected, in terms of total weight of the microcapsule, from 0.1% to 20.0 % by weight and preferably from 0.5% to 15% by weight. When the amount of the outmost shell is less than 0.1% by weight, the shell coating may be meaningless, and when it is more than 20.0% by weight, the feeling of the presence of foreign substances may be caused.

The thickness of the outmost shell is not particularly limited and may be suitably chosen according to the finally desired microcapsule. For example, the outmost shell may have a thickness which is larger than 20 μm, particularly 30 μm, preferably 40 μm, and more preferably 50 μm, and which is smaller than 200 μm, particularly 150 μm, preferably 120 μm, and more preferably 90 μm.

Other examples of polymers which could be implemented as the outmost shell will be given later during the description of the binder which may be used in the microcapsules of the present invention.

1-4-3. Process

The microcapsules may be produced by conventional methods known in the art within the coating or encapsulation domain, including pelletization, granulation, coating, etc. For example, the microcapsules may be obtained by the steps of containing a mixture of the compounds (actives, pigments, polymers, solvents) and drying to form capsules as disclosed in WO01/35933 and WO2011/027960, or the steps of granulation and coating by spray drying as disclosed in FR2841155, or by fluidized bed technology, which has been used in the food and pharmaceutical industry. An example may be cited in WO08/139053 for the preparation of a spheroid multilayer containing a core of sugar and concentric layers of pharmaceutical actives. Fixation of pharmaceutical actives on the core is made by impregnation or pulverization or projection, and then the first layer is dried before application of a second layer.

Preferably, the microcapsules introduced in the composition of the present invention are obtainable, and preferably obtained, at least in part, by fluidized bed technology which is described later. The fluid-bed process is characterized in that leads to real capsules compared to spray drying, which leads to granular particles formed by particle cohesion or to a matrix with the core material randomly dispersed in a polymer. In particular the use of a fluid-bed process allows substantially spherical microcapsules with a core substantially spherical, surrounded by at least one layer circumferentially surrounding the core and preferably at least one outer layer circumferentially surrounding the inner layer.

The fluid bed process is disclosed by example in 'Fluid-Bed Coating, Teunou, E.; Poncelet, 2005, D. *Food Science and Technology (BocaRaton, FL, United States)*, Volume 146, Issue

Encapsulated and Powdered Foods, Pages 197-212. A person skilled in the art knows how to adjust air quantity, liquid quantity and temperature allowing reproduction of the microcapsule according to the present invention.

Preferably a fluid bed process includes a Würster process and/or a tangential spray process. Such processes allow, contrary to a pelletization process, spherical capsules with a core surrounded by one or more circumferential layers.

By combining two or more compounds (e.g., polymers, lipid-based material) with titanium dioxide particles in the microcapsules of different hardness and/or water solubility, it is possible to adjust the time required for colorant-encapsulated microcapsules to break down on the skin so that, by varying the method or intensity of application onto the skin, it is possible to adjust the preferred coloration or gradation pattern.

Preferably, the multi-layered coating contains at least starch as a polymer with at least one lipid-based material and preferably lecithin.

Preferably, the microcapsules additionally include a lipid-based material chosen from phospholipids, advantageously selected from phosphoacylglycerol and in particular lecithins.

Preferably, the microcapsules include three or more different colorants (in terms of color). More preferably, the colorants are inorganic pigments, and even more preferably metal oxide(s).

In the present invention, an organic solvent may be employed in the preparation of a coating solution used in the fluidized bed coating process. The organic solvent is not specifically restricted but preferably includes methylene chloride, methanol, ethanol, and mixtures thereof. It is possible to employ any organic solvent if it can dissolve or disperse the polymers and/or lipid-based materials, has a boiling point less than that of water, and has a low residual toxicity.

The microcapsules used in the present invention are obtainable, and preferably obtained, by the following steps:
(a-1) preparing particles of a colored core (A-1) containing at least one colorant and at least one binder, and
(a-2) optionally coating the colored core prepared in the above step (a-1) with a solution in which a colorant and a binder that are the same as or different from those used in the above step (a-1) are dissolved or dispersed to form an inner color layer (A-2),
(b) coating the particles prepared in the above step (a-1) or (a-2) with a solution in which titanium dioxide particles and a binder form a pressure-breakable wall layer (B),
(c-1) optionally coating the particles obtained in the above step (b) with a solution in which a colorant and a binder that are the same as or different from those used in the above steps (a-1) or (a-2) are dissolved or dispersed to form an outer color layer (C-1),
(c-2) optionally coating the particles obtained in the above step (b) or (c-1) with a solution in which a shell-forming polymer is dissolved or dispersed to form an outmost shell.

The present invention will be further explained by the following examples, but is not restricted to them.

1-4-4 Properties of the microcapsules

The microcapsules are stable in the compositions of the present invention, preferably at high temperatures, for example greater than or equal to 40°C, for example for one month, better two months and still better three months in an oven at 45°C or for 15 days in an oven at 60°C.

Preferably, the microcapsules present appropriate softening kinetics. More preferably, at least three hours after being in contact with the other compounds of the formula, the hardness of the microcapsules is advantageously from 5 to 50 grams, more preferably from 6 to 20 grams and still more preferably from 7 to 10 grams. Such hardness is in conformity with an industrial process for preparing compositions including such microcapsules. Such values of softening kinetics and hardness allow the provision of not only aesthetic microcapsules but also overall aesthetic compositions.

Particularly, the composition may lead to different shades or color gradations depending on the intensity of the rubbing. The compositions may advantageously present a high chromaticity C* as measured in the in CIE Lab system 1976.

1-5. Additional Surfactant

The composition of the present invention may further contain at least one additional surfactant, in addition to (b) above. A single type of additional surfactant may be used, but two or more different types of additional surfactant may be used in combination.

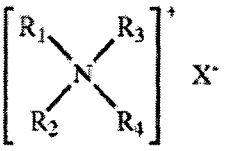
As the additional surfactant, at least one ionic surfactant may be used. The ionic surfactant can be selected from the group consisting of a cationic surfactant, an anionic surfactant, and an amphoteric surfactant, preferably selected from the group consisting of an anionic surfactant and an amphoteric surfactant, and more preferably an anionic surfactant.

1-5-1. Cationic surfactant

The cationic surfactant is not limited. The cationic surfactant may be selected from the group consisting optionally of polyoxyalkylenated, primary, secondary or tertiary fatty amine salts, quaternary ammonium salts, and mixtures thereof.

Examples of quaternary ammonium salts that may be mentioned include, but are not limited to,those of general formula (V) below:

[formula (V)]



(V)

wherein R_1, R_2, R_3, and R_4, which may be identical or different, are chosen from linear and branched aliphatic radicals containing from 1 to 30 carbon atoms and optionally containing heteroatoms such as oxygen, nitrogen, sulfur and halogens. The aliphatic radicals may be chosen, for example, from alkyl, alkoxy, C_2-C_6 polyoxyalkylene, alkylamide, (C_{12}-C_{22})alkylamido(C_2-C_6)alkyl, (C_{12}-C_{22})alkylacetate and hydroxyalkyl radicals; and aromatic radicals such as aryl and alkylaryl; and X^- is chosen from halides, phosphates, acetates, lactates, (C_2-C_6) alkyl sulfates and alkyl- or alkylaryl-sulfonates; quaternary ammonium salts of imidazoline; diquaternary ammonium salts; and quaternary ammonium salts containing at least one ester function.

The quaternary ammonium salts mentioned above that may be used in the compositions according to the present invention include, but are not limited to, tetraalkylammonium chlorides, for instance dialkyldimethylammonium and alkyltrimethylammonium chlorides in which the alkyl radical contains from about 12 to 22 carbon atoms, such as behenyltrimethylammonium, distearyldimethylammonium, cetyltrimethylammonium and benzyldimethylstearylammonium chloride; palmitylamidopropyltrimethylammonium chloride; and stearamidopropyldimethyl(myristyl acetate)ammonium chloride, sold under the name "Ceraphyl® 70" by the company Van Dyk.

In one embodiment, the cationic surfactant that may be used in the compositions of the present invention is chosen from quaternary ammonium salts, for example from behenyltrimethylammonium chloride, cetyltrimethylammonium chloride, Quaternium-83, Quaternium-87, Quaternium-22, behenylamidopropyl-2,3-dihydroxypropyldimethylammonium chloride, palmitylamidopropyltrimethylammonium chloride, and stearamidopropyldimethylamine.

1-5-2. Anionic surfactant

The anionic surfactant is not limited. The anionic surfactants may be chosen in particular from anionic derivatives of proteins of vegetable origin or of silk proteins, phosphates and alkyl phosphates, carboxylates, sulphosuccinates, amino acid derivatives, alkyl sulphates, alkyl ether sulphates, sulphonates, isethionates, taurates, alkyl sulphoacetates, polypeptides, anionic derivatives of alkyl polyglucosides, and their mixtures.

1) Anionic derivatives of proteins of vegetable origin are protein hydrolysates containing a hydrophobic group, it being possible for the hydrophobic group to be naturally present in the protein or to be added by reaction of the protein and/or of the protein hydrolysate with a hydrophobic compound. The proteins are of vegetable origin or derived from silk, and the

hydrophobic group can in particular be a fatty chain, for example an alkyl chain containing from 10 to 22 carbon atoms. Mention may more particularly be made, as anionic derivatives of proteins of vegetable origin, of apple, wheat, soybean or oat protein hydrolysates containing an alkyl chain having from 10 to 22 carbon atoms, and their salts. The alkyl chain can in particular be a lauryl chain and the salt can be a sodium, potassium and/or ammonium salt.

Thus, mention may be made, as protein hydrolysates containing a hydrophobic group, for example, of salts of protein hydrolysates where the protein is a silk protein modified by lauric acid, such as the product sold under the name Kawa Silk by Kawaken; salts of protein hydrolysates where the protein is a wheat protein modified by lauric acid, such as the potassium salt sold under the name Aminofoam W OR by Croda (CTFA name: potassium lauroyl wheat amino acids) and the sodium salt sold under the name Proteol LW 30 by Seppic (CTFA name: sodium lauroyl wheat amino acids); salts of protein hydrolysates where the protein is an oat protein containing an alkyl chain having from 10 to 22 carbon atoms and more especially salts of protein hydrolysates where the protein is an oat protein modified by lauric acid, such as the sodium salt sold under the name Proteol OAT (30% aqueous solution) by Seppic (CTFA name: sodium lauroyl oat amino acids); or salts of apple protein hydrolysates containing an alkyl chain having from 10 to 22 carbon atoms, such as the sodium salt sold under the name Proteol APL (30% aqueous/glycol solution) by Seppic (CTFA name: sodium cocoyl apple amino acids). Mention may also be made of a mixture of lauroyl amino acids (aspartic acid, glutamic acid, glycine, alanine) neutralized with sodium N-methylglycinate sold under the name Proteol SAV 50 S by Seppic (CTFA name: sodium cocoyl amino acids).

2) Mention may be made, as phosphates and alkyl phosphates, for example, of monoalkyl phosphates and dialkyl phosphates, such as lauryl monophosphate, sold under the name MAP 20® by Kao Chemicals, the potassium salt of dodecyl phosphate, the mixture of mono- and diesters (predominantly diester) sold under the name Crafol AP-31® by Cognis, the mixture of octyl phosphate monoester and diester, sold under the name Crafol AP-20® by Cognis, the mixture of ethoxylated (7 mol of EO) 2-butyloctyl phosphate monoester and diester, sold under the name Isofol 12 7 EO-Phosphate Ester® by Condea, the potassium or triethanolamine salt of mono(C_{12}-C_{13})alkyl phosphate, sold under the references Arlatone MAP 230K-40® and Arlatone MAP 230T-60® by Uniqema, potassium lauryl phosphate, sold under the name Dermalcare MAP XC-99/09® by Rhodia Chimie, and potassium cetyl phosphate, sold under the name Arlatone MAP 160K by Uniqema.

3) Mention may be made, as carboxylates, of:

- amido ether carboxylates (AEC), such as sodium lauryl amido ether carboxylate (3 EO), sold under the name Akypo Foam 30® by Kao Chemicals;
- polyoxyethylenated carboxylic acid salts, such as oxyethylenated (6 EO) sodium lauryl ether carboxylate (65/25/10 C_{12}-C_{14}-C_{16}), sold under the name Akypo Soft 45 NV® by Kao Chemicals, polyoxyethylenated and carboxymethylated fatty acids originating from olive oil, sold under the name Olivem 400® by Biologia E Tecnologia, or oxyethylenated (6 EO) sodium tridecyl ether carboxylate, sold under the name Nikkol ECTD-6NEX® by

Nikkol; and

- salts of fatty acids (soaps) having a C_6 to C_{22} alkyl chain which are neutralized with an organic or inorganic base, such as potassium hydroxide, sodium hydroxide, triethanolamine, N-methylglucamine, lysine and arginine.

4) Mention may in particular be made, as amino acid derivatives, of alkali salts of amino acids, such as:

- sarcosinates, such as sodium lauroyl sarcosinate, sold under the name Sarkosyl NL 97® by Ciba or sold under the name Oramix L 30® by Seppic, sodium myristoyl sarcosinate, sold under the name Nikkol Sarcosinate MN® by Nikkol, or sodium palmitoyl sarcosinate, sold under the name Nikkol Sarcosinate PN® by Nikkol;
- alaninates, such as sodium N-lauroyl-N-methylamidopropionate, sold under the name Sodium Nikkol Alaninate LN 30® by Nikkol or sold under the name Alanone ALE® by Kawaken, or triethanolamine N-lauroyl-N-methylalanine, sold under the name Alanone ALTA® by Kawaken;
- glutamates, such as triethanolamine monococoyl glutamate, sold under the name Acylglutamate CT-12® by Ajinomoto, triethanolamine lauroyl glutamate, sold under the name Acylglutamate LT-12® by Ajinomoto;
- aspartates, such as the mixture of triethanolamine N-lauroyl aspartate and triethanolamine N-myristoyl aspartate, sold under the name Asparack® by Mitsubishi;
- glycine derivatives (glycinates), such as sodium N-cocoyl glycinate, sold under the names Amilite GCS-12® and Amilite GCK 12 by Ajinomoto;
- citrates, such as the citric monoesters of oxyethylenated (9 mol) coco alcohols, sold under the name Witconol EC 1129 by Goldschmidt; and
- galacturonates, such as sodium dodecyl D-galactoside uronate, sold by Soliance.

5) Mention may be made, as sulphosuccinates, for example, of oxyethylenated (3 EO) lauryl (70/30 C_{12}/C_{14}) alcohol monosulphosuccinate, sold under the names Setacin 103 Special® and Rewopol SB-FA 30 K 4® by Witco, the disodium salt of a hemisulphosuccinate of C_{12}-C_{14} alcohols, sold under the name Setacin F Special Paste® by Zschimmer Schwarz, oxyethylenated (2 EO) disodium oleamidosulphosuccinate, sold under the name Standapol SH 135® by Cognis, oxyethylenated (5 EO) lauramide monosulphosuccinate, sold under the name Lebon A-5000® by Sanyo, the disodium salt of oxyethylenated (10 EO) lauryl citrate monosulphosuccinate, sold under the name Rewopol SB CS 50® by Witco, or ricinoleic monoethanolamide monosulphosuccinate, sold under the name Rewoderm S 1333® by Witco. Use may also be made of polydimethylsiloxane sulphosuccinates, such as disodium PEG-12 dimethicone sulphosuccinate, sold under the name Mackanate-DC 30 by MacIntyre.

6) Mention may be made, as alkyl sulphates, for example, of triethanolamine lauryl sulphate (CTFA name: TEA lauryl sulphate), such as the product sold by Huntsman under the name Empicol TL40 FL or the product sold by Cognis under the name Texapon T42, which products are at 40% in aqueous solution. Mention may also be made of ammonium lauryl sulphate (CTFA name: ammonium lauryl sulphate), such as the product sold by Huntsman under the

name Empicol AL 30FL, which is at 30% in aqueous solution.

7) Mention may be made, as alkyl ether sulphates, for example, of sodium lauryl ether sulphate (CTFA name: sodium laureth sulphate), such as that sold under the names Texapon N40 and Texapon AOS 225 UP by Cognis, or ammonium lauryl ether sulphate (CTFA name: ammonium laureth sulphate), such as that sold under the name Standapol EA-2 by Cognis.

8) Mention may be made, as sulphonates, for example, of α-olefinsulphonates, such as sodium α-olefinsulphonate (C_{14}-C_{16}), sold under the name Bio-Terge AS-40® by Stepan, sold under the names Witconate AOS Protégé® and Sulframine AOS PH 12® by Witco or sold under the name Bio-Terge AS-40 CG® by Stepan, secondary sodium olefinsulphonate, sold under the name Hostapur SAS 30® by Clariant; or linear alkylarylsulphonates, such as sodium xylenesulphonate, sold under the names Manrosol SXS30®, Manrosol SXS40® and Manrosol SXS93® by Manro.

9) Mention may be made, as isethionates, of acylisethionates, such as sodium cocoylisethionate, such as the product sold under the name Jordapon CI P® by Jordan.

10) Mention may be made, as taurates, of the sodium salt of palm kernel oil methyltaurate, sold under the name Hostapon CT Paté® by Clariant; N-acyl-N-methyltaurates, such as sodium N-cocoyl-N-methyltaurate, sold under the name Hostapon LT-SF® by Clariant or sold under the name Nikkol CMT-30-T® by Nikkol, Sodium Methyl Stearoyl Taurate sold under the name Nikkol SMT® or sodium palmitoyl methyltaurate, sold under the name Nikkol PMT® by Nikkol.

11) The anionic derivatives of alkyl polyglucosides can in particular be citrates, tartrates, sulphosuccinates, carbonates and glycerol ethers obtained from alkyl polyglucosides. Mention may be made, for example, of the sodium salt of cocoylpolyglucoside (1,4) tartaric ester, sold under the name Eucarol AGE-ET® by Cesalpinia, the disodium salt of cocoylpolyglucoside (1,4) sulphosuccinic ester, sold under the name Essai 512 MP® by Seppic, or the sodium salt of cocoylpolyglucoside (1,4) citric ester, sold under the name Eucarol AGE-EC® by Cesalpinia.

Preferably, the amino acid derivatives may be acyl glycine derivatives or glycine derivatives, in particular acyl glycine salt.

The acyl glycine derivatives or glycine derivatives can be chosen from acyl glycine salts (or acyl glycinates) or glycine salts (or glycinates), and in particular from the following.

i) Acyl glycinates of formula: R–$HNCH_2COOX$
in which

- R represents an acyl group R'C=O, with R', which represents a saturated or unsaturated, linear or branched, hydrocarbon chain, preferably containing from 10 to 30 carbon atoms, more preferably from 12 to 22 carbon atoms, even more preferably from 14 to 22 carbon

atoms and better still from 16 to 20 carbon atoms, and

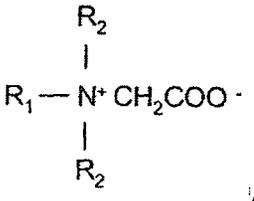
- X represents a cation chosen, for example, from the ions of alkali metals, such as Na, Li or K, preferably Na or K, the ions of alkaline earth metals, such as Mg, ammonium groups and their mixtures.

The acyl group can in particular be chosen from the lauroyl, myristoyl, behenoyl, palmitoyl, stearoyl, isostearoyl, olivoyl, cocoyl or oleoyl groups and their mixtures.

Preferably, R is a cocoyl group.

ii) Glycinates of following formula (VI):

[formula (VI)]



(VI)

in which:

- R_1 represents a saturated or unsaturated, linear or branched, hydrocarbon chain containing from 10 to 30 carbon atoms, preferably from 12 to 22 carbon atoms and better still from 16 to 20 carbon atoms; R_1 is advantageously chosen from the lauryl, myristyl, palmityl, stearyl, cetyl, cetearyl or oleyl groups and their mixtures and preferably from the stearyl and oleyl groups,
- the R_2 groups, which are identical or different, represent an R"OH group, R" being an alkyl group containing from 2 to 10 carbon atoms, preferably from 2 to 5 carbon atoms.

Mention may be made, as the compounds of formula (VI), for example, of the compounds carrying the INCI name sodium cocoyl glycinate, such as, for example, Amilite GCS-12, sold by Ajinomoto, or potassium cocoyl glycinate, such as, for example, Amilite GCK-12 from Ajinomoto.

Use may be made, as the compounds of formula (VI), of dihydroxyethyl oleyl glycinate or dihydroxyethyl stearyl glycinate.

1-5-3. Amphoteric surfactant

The amphoteric surfactant is not limited. The amphoteric or zwitterionic surfactants can be, for example (non-limiting list), amine derivatives such as aliphatic secondary or tertiary amine, and optionally quaternized amine derivatives, in which the aliphatic radical is a linear or branched chain containing 8 to 22 carbon atoms and containing at least one water-solubilizing anionic group (for example, carboxylate, sulphonate, sulphate, phosphate or phosphonate).

Among the amidoaminecarboxylated derivatives, mention may be made of the products sold under the name Miranol, as described in U.S. Pat. Nos. 2,528,378 and 2,781,354 and classified in the CTFA dictionary, 3rd edition, 1982 (the disclosures of which are incorporated herein by reference), under the names Amphocarboxyglycinates and Amphocarboxypropionates, with the respective structures:

R_1-$CONHCH_2CH_2$-$N^+(R_2)(R_3)(CH_2COO^-)$

in which: R_1 denotes an alkyl radical of an acid R_1-COOH present in hydrolysed coconut oil, a heptyl, nonyl or undecyl radical,

R_2 denotes a beta-hydroxyethyl group, and

R_3 denotes a carboxymethyl group; and

R_1'-$CONHCH_2CH_2$-N(B)(C)

in which: B represents -CH_2CH_2OX',

C represents -$(CH_2)_z$-Y', with z=1 or 2,

X' denotes a -CH_2CH_2-COOH group, -CH_2-COOZ', -CH_2CH_2-COOH, -CH_2CH_2-COOZ' or a hydrogen atom,

Y' denotes –COOH, –COOZ', -CH_2-CHOH-SO_3Z' or a -CH_2-CHOH-SO_3H radical,

Z' represents an ion of an alkaline or alkaline earth metal such as sodium, an ammonium ion or an ion issued from an organic amine, and

R_1' denotes an alkyl radical of an acid R_1'-COOH present in coconut oil or in hydrolysed linseed oil, an alkyl radical, such as a C_7, C_9, C_{11} or C_{13} alkyl radical, a C_{17} alkyl radical and its iso form, or an unsaturated C_{17} radical.

It is preferable that the amphoteric surfactant be selected from (C_8-C_{24})-alkyl amphomonoacetates, (C_8-C_{24})alkyl amphodiacetates, (C_8-C_{24})alkyl amphomonopropionates, and (C_8-C_{24})alkyl amphodipropionates.

These compounds are classified in the CTFA dictionary, 5th edition, 1993, under the names Disodium Cocoamphodiacetate, Disodium Lauroamphodiacetate, Disodium Caprylamphodiacetate, Disodium Capryloamphodiacetate, Disodium Cocoamphodipropionate, Disodium Lauroamphopropionate, Disodium Caprylamphodipropionate, Disodium Caprylamphodipropionate, Lauroamphodipropionic acid and Cocoamphodipropionic acid.

By way of example, mention may be made of the cocoamphodiacetate sold under the trade name Miranol® C2M concentrate by the company Rhodia Chimie.

Preferably, the amphoteric surfactant may be a betaine.

The betaine-type amphoteric surfactant is preferably selected from the group consisting of alkylbetaines, alkylamidoalkylbetaines, alkylsulfobetaines, alkylphosphobetaines, and alkylamidoalkylsulfobetaines, in particular, (C_8-C_{24})alkylbetaines, (C_8-C_{24})alkylamido(C_1-C_8)alkylbetaines, (C_8-C_{24})alkylsulphobetaines, and (C_8-C_{24})alkylamido(C_1-C_8)alkylsulphobetaines. In one embodiment, the amphoteric surfactants of betaine type are chosen from (C_8-C_{24})alkylbetaines,

(C_8-C_{24})alkylamido(C_1-C_8)alkylsulphobetaines, (C_8-C_{24})alkylsulphobetaines, and alkyl(C_8-C_{24})phosphobetaines.

Non-limiting examples that may be mentioned include the compounds classified in the CTFA dictionary, 9th edition, 2002, under the names cocobetaine, laurylbetaine, cetylbetaine, coco/oleamidopropylbetaine, cocamido propyl betaine, palmitamido propylbetaine, stearamidopropylbetaine, cocamidoethylbetaine, cocamidopropylhydroxysultaine, oleamidopropylhydroxysultaine, cocohydroxysultaine, laurylhydroxysultaine, and cocosultaine, alone or as mixtures.

The betaine-type amphoteric surfactant is preferably an alkylbetaine and an alkylamidoalkylbetaine, in particular cocobetaine and cocamidopropylbetaine.

The amount of the additional surfactant(s) may be, if used, 0.01% to 20% by weight, preferably 0.10% to 10% by weight, and more preferably from 1% to 5% by weight, relative to the total weight of the composition.

1-5-4. Polyol

The composition of the present invention may further contain at least one polyol. A single type of polyol may be used, but two or more different types of polyol may be used in combination.

The term "polyol" here means an alcohol having two or more hydroxy groups, and does not encompass a saccharide or a derivative thereof. The derivative of a saccharide includes a sugar alcohol which is obtained by reducing one or more carbonyl groups of a saccharide, as well as a saccharide or a sugar alcohol in which the hydrogen atom or atoms in one or more hydroxy groups thereof has or have been replaced with at least one substituent such as an alkyl group, a hydroxyalkyl group, an alkoxy group, an acylgroup or a carbonyl group.

The polyol may be a C_2-C_{12} polyol, preferably a C_{2-9} polyol, containing at least 2 hydroxy groups, and preferably 2 to 5 hydroxy groups.

The polyol may be a natural or synthetic polyol. The polyol may have a linear, branched or cyclic molecular structure.

The polyol may be selected from the group consisting of glycerins and glycols, more preferably propylene glycol, butylene glycol, pentylene glycol, hexylene glycol, dipropylene glycol, diethylene glycol, ethylhexylglycerine, caprylyl glycol, glycol ethers, preferably mono-, di- or tripropylene glycol of alkyl(C_1-C_4)ether or mono-, di- or triethylene glycol of alkyl(C_1-C_4)ether, and mixtures thereof, still more preferably the polyol is glycerol and/or butylene glycol.

The polyol may be present in an amount ranging from 0.01% to 30% by weight, and preferably from 0.1% to 20% by weight, such as from 1% to 10% by weight, relative to the total weight of

the composition.

1-5-5. Thickening agent

The composition of the present invention may further contain at least one thickening agent. A single type of thickening agent may be used, but two or more different types of thickening agent may be used in combination.

The thickeners may be chosen from below:
(i) associative thickeners, which is an amphiphilic thickener containing both hydrophilic units and hydrophobic units, for example, containing at least one C_8-C_{30} fatty chain and at least one hydrophilic unit;
(ii) crosslinked acrylic acid homopolymers;
(iii) crosslinked copolymers of (meth)acrylic acid and of (C_1-C_6)alkyl acrylate;
(iv) nonionic homopolymers and copolymers containing at least one of ethylenically unsaturated ester monomers and ethylenically unsaturated amide monomers;
(v) ammonium acrylate homopolymers and copolymers of ammonium acrylate and of acrylamide;
(vi) C_{12}-C_{30} fatty alcohols;
(vii) (un)modified carboxyvinyl polymers, such as the products sold under the name Carbopol (CTFA name: Carbomer) by the company Goodrich; polyacrylates;
(viii) polymethacrylates such as the products sold under the names Lubrajel and Norgel by the company Guardian or under the name Hispagel by the company Hispano Chimica;
(ix) polyacrylamides, optionally crosslinked;
(x) neutralized 2-acrylamido-2-methylpropanesulfonic acid polymers and copolymers, for instance the poly(2-acrylamido-2-methylpropanesulfonic acid) sold by the company Clariant under the name Hostacerin AMPS (CTFA name: ammonium polyacryldimethyltauramide);
(xi) crosslinked anionic copolymers of acrylamide and of AMPS, which are in the form of a W/O emulsion, such as those sold under the name Sepigel 305 (CTFA name: Polyacrylamide/C_{13}-C_{14} isoparaffin/Laureth-7) and under the name Simulgel 600 (CTFA name: Acrylamide/Sodium acryloyldimethyltaurate copolymer/Isohexadecane/Polysorbate 80) by the company SEPPIC;
(xii) polysaccharide biopolymers, for instance xanthan gum, guar gum, carob gum, acacia gum, scleroglucans, chitin and chitosan derivatives, carrageenans, gellans, alginates;
(xiii) celluloses such as microcrystalline cellulose, carboxymethylcellulose, hydroxymethylcellulose and hydroxypropylcellulose; and mixtures thereof, preferably chosen from Acrylates/C_{10}-C_{30} Alkyl Acrylate Crosspolymers such as, Carbopol ultrez 20, Carbopol ultrez 21, Permulen TR-1, Permulen TR-2, Carbopol 1382 , Carbopol ETD 2020, Carbomer such as Synthalen K, carbopol 980, Ammonium acryloyldimethyl Taurate/Steareth-8 Methacrylate copolymer such as Aristoflex SNC, Acrylate copolymers such as Carbopol Aqua SF-1, Ammonium acryloyldimethyl taurate/steareth-25 Methacrylate Crosspolymers such as Aristoflex HMS, Ammonium acryloyldimethyl taurate such as Arisfoflex AVC, and xanthan gum such as Keltrol CG;

and also any polymers which contribute not only to sustaining a proper viscosity, to further making capsule suspension very well and further to making it stable in terms of shelf life, but also to delivering transparency.

The thickening agent is preferably selected from associative thickeners, polysaccharides and (un)modified carboxyvinyl polymers such as starch, xanthene gum and Carbomer.

The viscosity of the composition of the present invention is not particularly limited. The viscosity can be measured at 25°C with viscosimeters or rheometers preferably with cone-plan geometry. Preferably, the viscosity of the composition of the present invention can range, for example, from 1 Pa.s to 2000 Pa.s, and preferably from 1 Pa.s to 1000 Pa.s at 25°C and 1 s^{-1}.

The thickening agent may be present in an amount ranging from 0.001% to 10% by weight, and preferably from 0.01% to 10% by weight, and still more preferably from 0.1% to 5% by weight, relative to the total weight of the composition.

1-5-6. Active agent

For applications in particular for caring for or making up the skin, the composition of the present invention may contain at least one active agent.

These active agent may be selected from the group consisting of a moisturizer, a sunscreen/sunblock agent, an anti-wrinkle agent, vitamins, (e.g., B3, B8, B12 and B9), a desquamating agent, a depigmenting agent, an antioxidant, etc.

For example, moisturizers (or humectants) that may especially be mentioned include sorbitol, polyhydric alcohols, preferably of C_2-C_8 and more preferably C_3-C_6, preferably such as glycerol, propylene glycol, 1,3-butylene glycol, pentylene glycol, hexylene glycol, dipropylene glycol, diethylene glycol and diglycerol, and mixtures thereof, glycerol and derivatives thereof, glycol ethers (especially containing from 3 to 16 carbon atoms) such as mono-, di- or tripropylene glycol (C_1-C_4)alkyl ethers, mono-, di- or triethylene glycol (C_1-C_4)alkyl ethers, urea and derivatives thereof, especially Hydrovance (2-hydroxyethylurea) sold by National Starch, lactic acids, hyaluronic acid, AHAs, BHAs, sodium pidolate, xylitol, serine, sodium lactate, ectoin and derivatives thereof, chitosan and derivatives thereof, collagen, plankton, an extract of *Imperata cylindra* sold under the name Moist 24 by the company Sederma, acrylic acid homopolymers, for instance Lipidure-HM® from NOF Corporation, beta-glucan and in particular sodium carboxymethyl beta-glucan from Mibelle-AG-Biochemistry; a mixture of passionflower oil, apricot oil, corn oil and rice bran oil sold by Nestle under the name NutraLipids®; a C-glycoside derivative such as those described in patent application WO 02/051 828 and in particular C-β-D-xylopyranoside-2-hydroxypropane in the form of a solution containing 30% by weight of active material in a water/propylene glycol mixture (60/40% by weight) such as the product manufactured by Chimex under the trade name Mexoryl SBB®; an oil of musk rose sold by Nestle; spheres of collagen and of chondroitin sulfate of marine origin (Atelocollagen) sold by the company Engelhard Lyon under the name Marine Filling Spheres; hyaluronic acid spheres

such as those sold by the company Engelhard Lyon; arginine, argan oil, and mixtures thereof.

Preferably, use will be made of a moisturizer chosen from glycerol, urea and derivatives thereof, especially Hydrovance® sold by National Starch, a C-glycoside derivative such as those described in patent application WO 02/051 828 and in particular C-β-D-xylopyranoside-2-hydroxypropane in the form of a solution containing 30% by weight of active material in a water/propylene glycol mixture (60/40% by weight) such as the product manufactured by Chimex under the trade name Mexoryl SBB®; argan oil, and mixtures thereof.

More preferably, glycerol will be used.

The moisturizer(s) may be present in the composition in an amount ranging from 0.1% to 15% by weight, especially from 0.5% to 10% by weight or even from 1% to 6% by weight, relative to the total weight of the said composition.

Sunscreens (or sunblocks) are important skin-care products to prevent from photoaging and skin cancer. There are two groups of sunscreens: UVA sunscreens, which typically block UV radiation in the wavelength range of 320 to 400 nm, and UVB sunscreens, which typically block radiation in the wavelength range of 290 to 320 nm.

The compositions of the present invention contain organic and/or inorganic UV sunscreen ingredients active in the UVA and/or UVB region which are hydrophilic and/or lipophilic. In particular, the UV sunscreen ingredients of the invention may have solubility from 8.0 to 9.5. Such UV sunscreen ingredients have a good plasticizer function.

Advantageously, the UV sunscreen agent of the present invention may have a molecular weight from 150 to 500 g/mol and contain hydrophobic sites and benzene nucleus or electron resonance group binding with polar sites.

The hydrophilic and/or lipophilic organic UV sunscreen ingredients are selected in particular from dibenzoylmethane derivatives; cinnamic derivatives; salicylic derivatives; benzophenone derivatives; β,β-diphenylacrylate derivatives; p-aminobenzoic acid (PABA) derivatives; and their mixtures.

Mention may be made, as examples of organic UV sunscreen ingredients, of those denoted below under their INCI names:
- para-Aminobenzoic acid derivatives:
- PABA,
- Ethyl PABA,
- Ethyl Dihydroxypropyl PABA,
- Ethylhexyl Dimethyl PABA, marketed in particular under the trademark "Escalol 507" by ISP,
- Glyceryl PABA,

- Dibenzoylmethane Derivatives:
- Butyl Methoxydibenzoylmethane, marketed in particular under the trademark "Parsol 1789" by Hoffmann-LaRoche,
- Isopropyl Dibenzoylmethane,
- Salicylic Derivatives:
- Homosalate, marketed under the trademark "Eusolex HMS" by Rona/EM Industries,
- Ethylhexyl Salicylate, marketed under the trademark "Neo Heliopan OS" by Haarmann and Reimer,
- Dipropyleneglycol Salicylate, marketed under the trademark "Dipsal" by Scher,
- TEA Salicylate, marketed under the trademark "Neo Heliopan TS" by Haarmann and Reimer,
- Cinnamic Derivatives:
- Ethylhexyl Methoxycinnamate, marketed in particular under the trademark "Parsol MCX" by Hoffmann-LaRoche,
- Isopropyl Methoxycinnamate,
- Isoamyl Methoxycinnamate, marketed under the trademark "Neo Heliopan E 1000" by Haarmann and Reimer,
- Cinoxate,
- DEA Methoxycinnamate,
- Diisopropyl Methylcinnamate,
- Glyceryl Ethylhexanoate Dimethoxycinnamate,
- β,β-Diphenylacrylate Derivatives:
- Octocrylene, marketed in particular under the trademark "Uvinul N539" by BASF,
- Etocrylene, marketed in particular under the trademark "Uvinul N35" by BASF,
- Benzophenone Derivatives:
- Benzophenone-1, marketed under the trademark "Uvinul 400" by BASF,
- Benzophenone-2, marketed under the trademark "Uvinul D50" by BASF,
- Benzophenone-3 or Oxybenzone, marketed under the trademark "Uvinul M40" by BASF,
- Benzophenone-4, marketed under the trademark "Uvinul MS40" by BASF,
- Benzophenone-5,
- Benzophenone-6, marketed under the trademark "Helisorb 11" by Norquay,

and their mixtures.

The preferred UV sunscreen ingredients are selected from the group consisting of cinnamic derivatives, β,β diphenylacrylates derivatives, salicylic derivatives, and their mixtures.

The preferred UV sunscreen ingredients are especially selected from the group consisting of ethylhexyl methoxycinnamate, octocrylene and ethylhexyl salicylate, and their mixtures.

Mention may be made especially of ethylhexyl methoxycinnamate sold under the tradename UVINUL MC 80® by the company BASF, of ethylhexyl salicylate sold under the tradename NEO HELIOPAN OS® by the company SYMRISE and of octocrylene sold under the tradename NEO HELIOPAN 303® by the company SYMRISE.

The composition of the present invention may contain from 0.1% to 30% by weight, for example from 0.5% to 20% by weight, for example from 1% to 15% by weight, and for example at least 1% by weight, of UV sunscreen ingredient relative to the total weight of the composition.

Anti-wrinkle agents: mention may be made of ascorbic acid and derivatives thereof, such as magnesium ascorbyl phosphate and ascorbyl glucoside; tocopherol and derivatives thereof, such as tocopheryl acetate; nicotinic acid and precursors thereof, such as nicotinamide; ubiquinone; glutathione and precursors thereof, such as L-2-oxothiazolidine-4-carboxylic acid; C-glycoside compounds and derivatives thereof, as described in particular hereinafter: extracts of plants, and in particular extracts of sea fennel and of olive leaf; and also plant proteins and hydrolysates thereof, such as rice or soybean protein hydrolysates; algal extracts and in particular of laminaria; bacterial extracts; sapogenins, such as diosgenin and extracts of Dioscorea plants, in particular of wild yam, containing them; α-hydroxy acids; β-hydroxy acids, such as salicylic acid and 5-n-octanoylsalicylic acid; oligopeptides and pseudodipeptides and acyl derivatives thereof, in particular {2-[acetyl-(3-trifluoromethylphenyl)amino]-3-methylbutyrylamino}acetic acid and the lipopeptides sold by the company Sederma under the trade names Matrixyl 500 and Matrixyl 3000; lycopene; manganese salts and magnesium salts, in particular manganese and magnesium gluconates; and mixtures thereof;

Desquamating agents: mention may be made of beta-hydroxy acids, in particular salicylic acids and derivatives thereof other than 5-n-octanoylsalicylic acid; urea; glycolic acid, citric acid, lactic acid, tartaric acid, malic acid or mandelic acid; 4-(2-hydroxyethyl)piperazine-1-propanesulphonic acid (HEPES); extract of Saphora japonica; honey; N-acetylglucosamine; sodium methylglycine diacetate, alpha-hydroxy acids (AHAs), beta-hydroxy acids (BHAs), and mixtures thereof;

Depigmenting agents: mention may be made of ceramides, vitamin C and derivatives thereof, in particular vitamin CG, CP and 3-O ethyl vitamin C, alpha- and beta-arbutin, ferulic acid, kojic acid, resorcinol and derivatives thereof, calcium D-pantetheine sulphonate, lipoic acid, ellagic acid, vitamin B3, phenylethyl resorcinol, for instance Symwhite 377® from the company Symrise, a kiwi fruit (*Actinidia chinensis*) juice sold by Gattefosse, an extract of *Paeonia suffructicosa* root, such as the product sold by the company Ichimaru Pharcos under the name Botanpi Liquid B®, an extract of brown sugar (*Saccharum officinarum*), such as the extract of molasses sold by the company Taiyo Kagaku under the name Molasses Liquid, a mixture of undecylenic acid and undecylenoyl phenyl alanine, such as Sepiwhite MSH® from Seppic;

Antioxidants: mention may more particularly be made of tocopherol and esters thereof, in particular tocopheryl acetate; EDTA, ascorbic acid and derivatives thereof, in particular magnesium ascorbyl phosphate and ascorbyl glucoside; chelating agents, such as BHT, BHA, N,N'-bis(3,4,5-trimethoxybenzyl)ethylenediamine and its salts, and mixtures thereof.

These active agents may be present in the composition in an amount ranging from 0.001% to 20% by weight, preferably from 0.01% to 10% by weight, and more preferably from 0.01% to 5% by weight, relative to the total weight of the composition.

1-6. Preparation and Properties of the Composition

The composition of the present invention can be prepared by mixing the above ingredients in accordance with a conventional process. The conventional process includes mixing with a high pressure homogenizer (a high energy process). Alternatively, the composition can be prepared by low energy processes such as a phase inversion temperature process (PIT), phase inversion concentration (PIC), autoemulsification, and the like. Preferably, the composition is prepared by a low energy process.

The ratio of the nonionic surfactant to the oil may be from 0.25 to 6, preferably from 0.3 to 3, and more preferably from 0.4 to 1.5.

The composition of the present invention is in the form of a nano- or micro-emulsion. The "micro-emulsion" may be referred to in two ways, namely, in a broader sense and in a narrower sense. That is to say, there is one case ("micro-emulsion in the narrow sense") in which the micro-emulsion refers to a thermodynamically stable isotropic single liquid phase containing a ternary system having three ingredients of an oily component, an aqueous component and a surfactant, and there is the other case ("micro-emulsion in the broad sense") in which, among thermodynamically unstable typical emulsion systems, the microemulsion additionally includes those such emulsions presenting transparent or translucent appearances due to their smaller particle sizes (Satoshi Tomomasa, et al., Oil Chemistry, Vol. 37, No. 11 (1988), pp. 48-53). "Micro-emulsion" as used herein refers to a "micro-emulsion in the narrow sense,", i.e., a thermodynamically stable isotropic single liquid phase.

The micro-emulsion refers to either one state of an O/W (oil-in-water) type micro-emulsion in which oil is solubilized by micelles, a W/O (water-in-oil) type micro-emulsion in which water is solubilized by reverse micelles, or a bicontinuous microemulsion in which the number of associations of surfactant molecules are rendered infinite so that both the aqueous phase and oil phase have a continuous structure.

The micro-emulsion may have a dispersed phase with a number average diameter of 100 nm or less, preferably 50 nm or less, and more preferably 20 nm or less, measured by laser granulometry.

"Nano-emulsion" here means an emulsion characterized by a dispersed phase with a size of less than 350 nm, the dispersed phase being stabilized by a crown of the nonionic surfactant that may optionally form a liquid crystal phase of lamellar type, at the dispersed phase/continuous phase interface. In the absence of specific opacifiers, the transparency of the nano-emulsions arises from the small size of the dispersed phase, this small size being obtained by virtue of the use of mechanical energy and especially a high-pressure homogenizer.

Nano-emulsions can be distinguished from micro-emulsions by their structure. Specifically, micro-emulsions are thermodynamically stable dispersions formed from, for example, the nonionic surfactant micelles swollen with the oil. Furthermore, micro-emulsions do not require substantial mechanical energy in order to be prepared.

The micro-emulsion may have a dispersed phase with a number average diameter of 300 nm or less, preferably 200 nm or less, and more preferably 150 nm or less, measured by laser granulometry.

The composition of the present invention may be in the form of an O/W nano- or micro-emulsion, a W/O nano- or micro-emulsion or a bicontinuous emulsion. Preferably, the composition of the present invention is in the form of an O/W nano- or micro-emulsion.

In a preferable embodiment, the composition of the present invention may be in the form of an O/W emulsion. In this case, the oil may be in the form of droplets with a number average particle size of 300 nm or less, preferably from 10 nm to 200 nm, and more preferably from 20 nm to 150 nm.

The mean size of the droplets of the oil phase is measured by light diffraction using a Mastersizer 2000 particle sizer (sold by Malvern Instruments). These measurements are carried out on the emulsion diluted in a solution of SDS (sodium dodecyl sulphate) at 1% in water. A computer program makes it possible to obtain the mean diameter by volume D[4.3] (μm) (see operators guide, Malvern Instruments, December 1998, p. 61 to 67).

The mean size D[4.3] (μm) of the droplets of the oil phase of the composition of the present invention ranges from 10 nm to 150 nm, and more preferably from 20 nm to 140 nm.

The compositions of the present invention are notably stable, particularly during 2 months at room temperature and even at 37°C or 45°C under atmospheric pressure and they present optimal cosmetic properties. Indeed the compositions of the present invention present an appropriate fluidity: they are easy to handle and further easy to apply and to spread on the skin.

These compositions also present a required texture for cosmetic use: they are not sticky, are soft to the touch and impart resilient feeling. Therefore, the compositions of the present invention also have the advantage of satisfying consumer expectations in terms of cosmeticity, such as lower viscosity and better emolliency.

The composition of the present invention may be a "color-changing composition". The term "color-changing composition" means a composition wherein the color before application is different from the color after application, this difference being visible to the naked eye.

In particular, this color-changing composition may be linked to a color-difference ΔE under the

CIE Lab system 1976 (ΔE before/after application) values. ΔE is defined by the equation:

[Math. 1]

$$\Delta E^* = \sqrt{((L_1 - L_2)^2 + (a_1 - a_2)^2 + (b_1 - b_2)^2}:$$

wherein L_1, a_1, b_1 are the parameters in the colorimetric space of the first color (composition before application) and L_2, a_2, b_2 are the parameters for the second color (composition after the application and homogenization on the keratinous material). These values may be measured by spectrophotometer or with a Chromasphere (for compositions applied on the skin). The color changing composition of the present invention may be characterized as having a ΔE before/after application greater than 1, in particular greater than or equal to 2, preferably greater than or equal to 3.

The composition of the present invention can have a transparent or slightly translucent appearance, preferably a transparent appearance. In other words, the composition of the present invention contains microcapsules containing releasable colorant(s) in a transparent medium.

The transparency may be measured by measuring the transmittance with an absorption spectrometer in the visible region (for example, transparency was measured with a V-550 (JASCO) with a 2 mm width cell as an average of visible light transmittance (between 400 and 800 nm)). The measurement is taken on the undiluted composition. The blank is determined with distilled water.

The composition of the present invention may preferably have a transparency greater than 50%, preferably greater than 60%, more preferably greater than 70%, and even more preferably greater than 75%.

In a preferred embodiment, the composition of the present invention contains microcapsules; preferably uncolored microcapsules, the outer layer being white or transparent, and when the outer layer is transparent, the visible inner layer is white. For the purposes of the present invention, the term "transparent composition" means a composition which transmits at least 40% of light at a wavelength of 750 nm without scattering the light, i.e., a composition in which the scattering angle of the light is less than 50° and is better still about 5° . The transparent composition may transmit at least 50%, especially at least 60% and especially at least 70% of light at a wavelength of 750 nm.

The light transmission measurement is made with a Cary 300 Scan UV-visible spectrophotometer from the company Varian, according to the following protocol:
- the composition is poured into a square-sided spectrophotometer cuvette with a side length of 10 mm;
- the sample of the composition is then maintained in a thermostatically regulated chamber at 20°C for 24 hours;

- the light transmitted through the sample of the composition is then measured on the spectrophotometer by scanning wavelengths ranging from 700 nm to 800 nm, the measurement being made in transmission mode;
- the percentage of light transmitted through the sample of the composition at a wavelength of 750 nm is then determined.

The transparent compositions, when they are placed 0.01 m in front of a black line 2 mm thick in diameter drawn on a sheet of white paper, allow this line to be seen; in contrast, an opaque composition, i.e., a non-transparent composition, does not allow the line to be seen.

The composition of the present invention, preferably a makeup foundation or a skin coloring product, provides a strong moisturizing sensation, creamy texture with very comfortable feeling during application, and sheer natural makeup result after application. In the end, all these features help to deliver a very good balance of skincare efficacy perception (creaminess and, moisturization) as well as makeup efficacy (proper coverage and natural radiance). Moreover the composition of the present invention may present a sunscreen effect. Advantageously the microcapsules are deformable in the presence of the aqueous phase. Advantageously the microcapsules inside the composition are breakable under pressure at the application on the keratinous materials.

2. Process and Use

The present invention also relates to a cosmetic process of applying the composition as described hereinbefore to the skin, the hair, mucous membranes, the nails, the eyelashes, the eyebrows or the scalp.

The present invention also relates to use of the composition as described hereinbefore, as or in care products and/or washing products and/or makeup products and/or makeup-removing products for the body and/or facial skin and/or mucous membranes and/or the scalp and/or the hair and/or the nails and/or the eyelashes and/or the eyebrows.

In other words, the composition of the present invention can be used, as it is, as the above product. Alternatively, the composition of the present invention can be used as an element of the above product. For example, the composition of the present invention can be added to or combined with any other elements to form the above product.

These compositions are prepared according to conventional methods. The compositions of this type may be in the form of a facial and/or body care or makeup product, and may be conditioned, for example, in the form of cream in a jar or of fluid in a tube or a pump-action bottle.

In a specific embodiment, the composition contains at least one neutralized 2-acrylamido-2-methylpropanesulfonic acid polymers and copolymers and one polysaccharide biopolymer.

The expression "transparent aqueous medium" means a medium allowing light to pass without causing deviation by refraction or reflection. The transparency of the aqueous medium can be measured using a turbidimeter. The portable Turbidimeter 2100P® Model from HACH company may be used, for example, for measuring the ranges of transparency of the composition. The composition is considered to be transparent when the measured value of turbidity is between 0 and 250 NTU and is considered as translucent for a value of turbidity from 250 to 1000 NTU.

The compositions, when placed in front of a 0.01 m thick black line with diameter of 2 mm drawn on a white sheet, reveal this black line, as opposed to an opaque composition that is to say, not transparent which would not allow it. The composition of the present invention preferably contains water and multilayered microcapsules containing releasable colorant(s). In a preferred embodiment, the composition of the present invention contains at least one hydrophilic or lipophilic gelling agent and at least one water soluble emollient(s) and/or lipid(s) with a polar moiety. In a preferred embodiment, the composition of the present invention contains at least two types of different multilayered microcapsules containing releasable colorant(s).

Microcapsules may be introduced in the last step with gentle stirring without damaging the microcapsules after a gel is made.

Such obtained transparent compositions with microcapsules present a pure and clean appearance, with perfect stability under -20/20°C (5 cycles), room temperature (25°C, 2 months), 37°C (2 months) and 45°C (2 months) under atmospheric pressure. The microcapsules release pigments during application without any particles being felt. Makeup results are perfectly and evenly provided after application.

The composition of the present invention is preferably transparent, and may also be slightly colored. In this case, the composition of the present invention contains at least one non-entrapped colorant, preferably in an amount of less than 1% by weight based on the total weight of the total composition.

The composition of the present invention may also be in the form of a jelly cream, or emulsified gel, containing oils and surfactants.

In another embodiment, the present invention relates to a kit containing one of the products defined above and an applicator. The applicator can be chosen from conventionally used applicators.

The composition of the invention can be applied, e.g., by finger or using an applicator. The container is preferably used in combination with an applicator containing at least one application component configured in order to apply the composition to keratinous substances.

This composition mainly contains water, at least one non-volatile oil, at least one O/W emulsifier and microcapsules.

Throughout the description, including the claims, the term "containing a" and "comprising a" should be understood as being synonymous with "containing at least one" and "comprising at least one" respectively, unless otherwise mentioned.

The terms "between... and..." and "from... to..." should be understood as being inclusive of the limits, unless otherwise specified.

The invention is illustrated in greater detail by the examples described below. Unless otherwise mentioned, the amounts indicated are expressed as mass percentages of active material.

EXAMPLES

The present invention will be described in more detail by way of examples, which however should not be construed as limiting the scope of the present invention.

Formulation Example

	Ex. 1	Comp. Ex. 1	Comp. Ex. 2
Polyglyceryl-5 Laurate(1) (nonionic surfactant)	3.00%	3.00%	0.00%
Na Methyl Stearoyl Taurate (anionic surfactant)	0.20%	0.20%	0.00%
Ethylhexyl Palmitate (oil)	3.00%	3.00%	0.00%
Acrylates/C10-30 alkyl acrylate crosspolymer	0.50%	0.50%	0.50%
Glycerin	10.00%	10.00%	10.00%
Butylene Glycol	5.00%	5.00%	5.00%
Microcapsule (2)	5.00%	0.00%	5.00%
Preservative	0.50%	0.50%	0.50%
Water	q.s.	q.s.	q.s.

1: SUNSOFT A-121E (by Taiyo Kagaku)
2: MAGIC30-BW0105 (by KPT)

(1) Preparation of compositions
Ex. 1, and Comp. Ex. 1 were formulated according to the following process:
An oil phase (a mixture of Ethylhexyl Palmitate + Polyglyceryl-5 Laurate + preservative) was prepared and the oil phase was heated up to around 75°C. Next, an aqueous phase (water + Na Methyl Stearoyl Taurate + Glycerin + Butylene Glycol) was prepared and the aqueous phase was heated up to around 75°C. Then, the aqueous phase was added into the oil phase.

After completing emulsification, to the mixture was added a thickener phase (Acrylates/C10-30 alkyl acrylate crosspolymer). Then the mixture was cooled down to room temperature. For Ex. 1, to the mixture was added MAGIC30-BW0105 at room temperature.

Comp. Ex. 2 was formulated according to the following process:
An aqueous phase (water + Glycerin + Butylene Glycol) was prepared and the aqueous phase was heated up to around 75°C. To the mixture was added a thickener phase (Acrylates/C10-30 alkyl acrylate crosspolymer). Then the mixture was cooled down to room temperature. To the mixture was added MAGIC30-BW0105 at room temperature.

(2) Evaluation of technical effect
(i) Observation (appearance)
The appearance was evaluated by visual observation.
(ii) Transparency for bulk without MAGIC30-BW0105
The transparency was measured with a V-550 (JASCO) with a 2 mm width cell. Transparency = average of Visible light transmittance (between 400 and 800 nm).
(iii) Particle Size
The particle size was measured with a VASCO-2 (CORDOUAN TECHNOLOGIES) at a non diluted condition. A computer program makes it possible to obtain the mean diameter by specifying intensity.
(iv) Coverage
The application color was measured at 1 mg/cm^3 of thickness on black Bioskin®. The value is shown by Δ L*. The lower the Δ L* value is, the more coverage is achieved.
(v) Sensorial test
In order to evaluate cosmeticity, a sensory test was conducted by 5 expert panelists. The panelists evaluated each composition in terms of emolliency and wetness in 5 grades.

Emolliency
5: very emollient
4: fairly emollient
3: relatively emollient
2: not emollient
1: very unemollient (skin feels rather harder)

Wetness
5: very wet
4: fairly wet
3: relatively wet
2: not wet
1: very unwet

TABLE 1

	Ex. 1	Comp. Ex. 1	Comp. Ex. 2
Aspect	Transparent to translucent gel with gray beads	Transparent to translucent gel	Transparent gel with gray beads
Transparency (%)	Not measurable	77.3%	Not measurable
Particle Size (nm)	147.30	177.88	Not Detected
Coverage (Δ L*)	-9.26	0	-2.46
Sensorial Emolliency (n=5)	4.2	-	2.4
Sensorial Wetness (n=5)	4.2	-	3

Mode of application on keratinous materials with observed technical effect

As is clear from the above results, it was found that the cosmetic composition in the form of an O/W emulsion according to the present invention had smaller oil droplets, and therefore, an aspect with better transparency was provided in the presence of microcapsules.

Comp. Ex. 1 is a formulation for comparison with Ex. 1 in that Comp. Ex. 1 lacks microcapsules. From the comparison between Ex. 1 and Comp. Ex. 1 it is inducible that Ex. 1 according to the present invention achieves a transparent gel in the presence of microcapsules, and the transparency is parity to the formulation lacking in microcapsules. The particle size of Ex. 1 is below 150 nm, and the composition is a nanoemulsion.

Comp. Ex. 2 is a formulation of an aqueous transparent gel. It means that Ex. 1 (transparent nanoemulsion gel) exceeds Comp. Ex. 2 (transparent aqueous gel) in coverage, and sensorial property (emolliency and wetness).

Claims

What is claimed is:

1. A composition in the form of a nano- or micro-emulsion, comprising:
   (a) at least one fatty phase;
   (b) at least one nonionic surfactant;
   (c) at least one microcapsule comprising releasable colorant(s); and
   (d) at least one aqueous phase.

2. The composition according to claim 1, which is an o/w emulsion.

3. The composition according to claim 1 or 2, further comprising at least one polyol, preferably selected from the group consisting of glycerins and glycols, more preferably propylene glycol, butylene glycol, pentylene glycol, hexylene glycol, dipropylene glycol, diethylene glycol, ethylhexylglycerine, caprylyl glycol, glycol ethers, preferably mono-, di- or tripropylene glycol of alkyl(C_1-C_4)ether or mono-, di- or triethylene glycol of alkyl(C_1-C_4)ether, and mixtures thereof, still more preferably the polyol is glycerol and/or butylene glycol.

4. The composition according to any one of claims 1 to 3, wherein the nonionic surfactant is selected from the group consisting of mono- or polyoxyalkylenated fatty acid esters, a polyglyceryl fatty ester surfactant, and fatty acid esters of sugars, especially of sucrose.

5. The composition according to claim 4, wherein the polyglyceryl fatty ester is with a polyglyceryl moiety derived from 4 to 6 glycerins, more preferably from 5 or 6 glycerins.

6. The composition according to any one of claims 1 to 5, wherein the amount of nonionic surfactant is from 0.1% to 30% by weight, preferably from 0.5% to 15% by weight, and more preferably from 1% to 10% by weight, relative to the total weight of the composition.

7. The composition according to any one of claims 1 to 6, wherein the fatty phase comprises an oil phase and the oil is selected from the group consisting of plant oils, animal oils, mineral oils, synthetic oils, silicone oils and hydrocarbon oils, preferably hydrocarbon oils selected from the group consisting of ester oil, ether oil, alkane oil, triglyceride oil, still more preferably an oil having a molecular weight below 700.

8. The composition according to of claim 7, wherein the amount of the oil is from 0.1% to 50% by weight, preferably from 0.5% to 40% by weight, and more preferably from 5% to 30% by weight, relative to the total weight of the composition.

9. The composition according to any one of claims 1 to 8, further comprising a thickener, preferably selected from the group consisting of
(i) associative thickeners; (ii) crosslinked acrylic acid homopolymers; (iii) crosslinked copolymers of (meth)acrylic acid and of (C_1-C_6)alkyl acrylate; (iv) nonionic homopolymers and

copolymers containing at least one of ethylenically unsaturated ester monomers and ethylenically unsaturated amide monomers; (v) ammonium acrylate homopolymers and copolymers of ammonium acrylate and of acrylamide; (vi) C_{12}-C_{30} fatty alcohols; (vii) (un)modified carboxyvinyl polymers; (viii) polymethacrylates; (ix) polyacrylamides, optionally crosslinked; (x) neutralized 2-acrylamido-2-methylpropanesulfonic acid polymers and copolymers; (xi) crosslinked anionic copolymers of acrylamide and of AMPS, which are in the form of a W/O emulsion; (xii) polysaccharide biopolymers; (xiii) celluloses, more preferably selected from the group consisting of (i) an associative thickener, (vii) (un)modified carboxyvinyl polymers and (ix) polysaccharide.

10. The composition according to any one of claims 1 to 9, wherein water is present in an amount ranging from 5% to 99% by weight, preferably from 10% to 95% by weight and still more preferably from 15% to 90% by weight relative to the total weight of the composition.

11. The composition according to any one of claims 1 to 10, wherein the microcapsule comprises
(A) a core, preferably uncolored core, comprising one organic material, and
(B) at least one layered coating surrounding the core, the layered coating comprising at least one polymer, at least one colorant, and advantageously at least one binder.

12. The composition according to any one of claims 1 to 11, comprising from 0.1% to 20% by weight and preferably from 0.5% to 15% by weight, and more preferably from 2% to 10% by weight of the (c) microcapsule relative to the total weight of the composition.

13. The composition according to any one of claims 1 to 12, wherein the core of the (c) microcapsules, comprises at least one monosaccharide or its derivatives as the organic material, in particular a monosaccharide-polyol advantageously selected from the group consisting of mannitol, erythritol, xylitol, sorbitol and mixtures thereof, preferably mannitol.

14. The composition according to anyone of claims 1 to 13, wherein the (c) microcapsules comprise at least:
- an inner core made of a monosaccharide-polyol, preferably mannitol,
- at least two layers of different color from each other,
- at least one hydrophilic polymer preferably selected from polysaccharides or their derivatives, and more preferably from starch or its derivatives, and advantageously at least one lipid based material, preferably an amphiphilic compound, more preferably a phospholipid, and even more preferably phosphoacylglycerol such as hydrogenated lecithin.

15. The composition according to any one of claims 1 to 14, wherein the (c) microcapsules comprise:
a) a core (A), preferably having a size less than 800 μm, more preferably less than about 400 μm, advantageously from 1 μm to 300 μm, in particular from 5 μm to 200 μm, and even more particularly from 10 μm to 100 μm in diameter, which preferably does not contain any colorant,

and comprising at least one organic core preferably selected from at least one sugar alcohol preferably a monosaccharide-polyol advantageously selected from the group consisting of mannitol, erythritol, xylitol, and sorbitol;
b) one first layer (B) surrounding the core comprising:
- at least one colorant, preferably iron oxide(s), and
- a binder selected from the group consisting of a polymer and a lipid-based material, preferably their mixture;
c) one second layer (C) surrounding said first layer (B), preferably having a thickness of 5 μm to 500 μm, comprising:
- titanium dioxide particles, and
- a binder selected from the group consisting of a polymer and a lipid-based material, preferably their mixture;
d) optionally one third layer (D) surrounding the second layer (C) comprising:
- at least one colorant, and
- a binder selected from the group consisting of a polymer and a lipid-based material, preferably their mixture;
e) optionally one fourth layer (E) surrounding the third layer (D), if any, or surrounding the second layer (C) comprising:
- at least one wall-forming polymer preferably selected from polysaccharides such as cellulose derivatives, in particular cellulose ether and cellulose ester, from (poly)(alkyl)(meth)acrylic acid and its derivatives, notably (poly)(alkyl)(meth)acrylate and its derivatives, and preferably from alkylacrylic/alkylmethacrylic acid copolymers and their derivatives.

16. The composition according to any one of claims 1 to 15, wherein the microcapsules inside the composition are breakable under pressure at the application on the keratinous materials.

17. The composition according to any one of claims 1 to 16, wherein the core represents from 10% to 90% by weight, preferably 20% to 80% by weight, more preferably from 30% to 70% by weight, and still more preferably from 40% to 60% by weight, relative to the total weight of the microcapsule.

18. The composition according to any one of claims 1 to 17, wherein the colorant represents from 20% to 90%, preferably from 30% to 80%; and in particular from 50% to 75% by weight relative to the microcapsule.

19. The composition according to any one of claims 1 to 18, wherein the colorants present in the microcapsules are selected from a group consisting of inorganic pigments, organic pigments and their mixture, preferably is at least one inorganic pigment, more preferably at least a mixture of inorganic pigments, even more preferably selected from metallic oxides, and in particular from iron oxide(s), titanium dioxide particles and their mixtures, preferably their mixture.

20. The composition according to any one of claims 1 to 10, wherein the microcapsule comprises:
(A) a core, having preferably a size ranging from 20 μm to 800 μm, comprising at least one colorant and preferably at least one binder, the colorant(s) including preferably at least one inorganic pigment preferably selected from iron oxide(s), and
(B) a pressure-breakable wall layer surrounding the core, comprising at least one colorant and preferably at least one binder, the colorant(s) comprising preferably at least titanium dioxide particles,
wherein the microcapsules include at least 70% by weight of colorant(s), compared to the total weight of the microcapsules.

21. The composition according to any one of claims 1 to 20, wherein at least one layer of the microcapsules is obtained by a fluid bed process.

22. A cosmetic process for caring for and/or making up keratinous materials, comprising application on the keratinous materials in particular on the skin of a composition according to any one of claims 1 to 21.

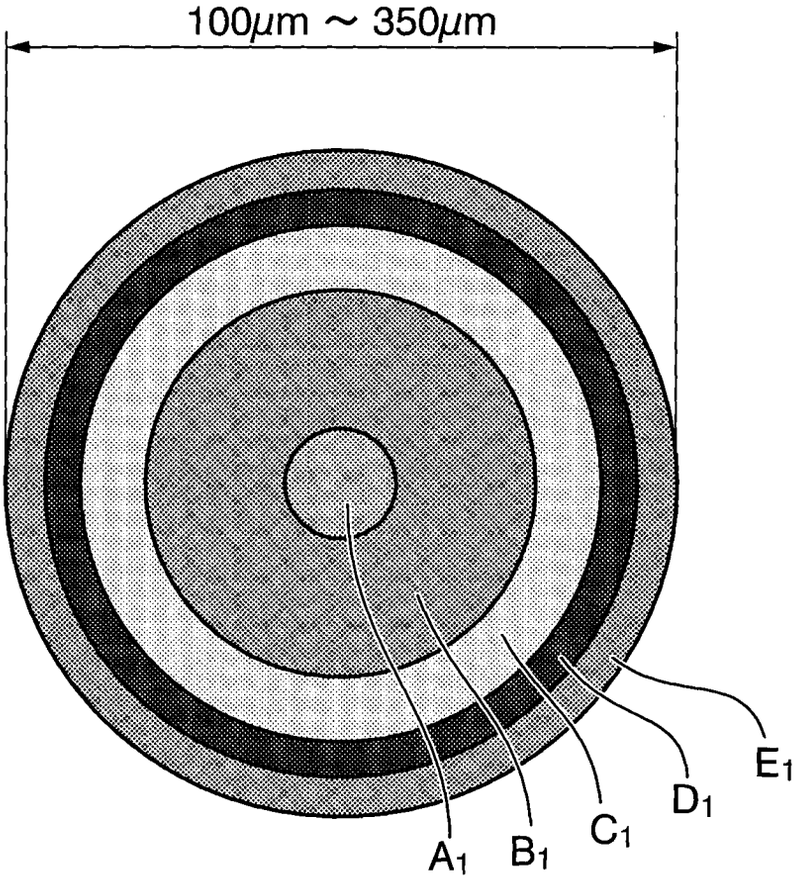


Figure 1

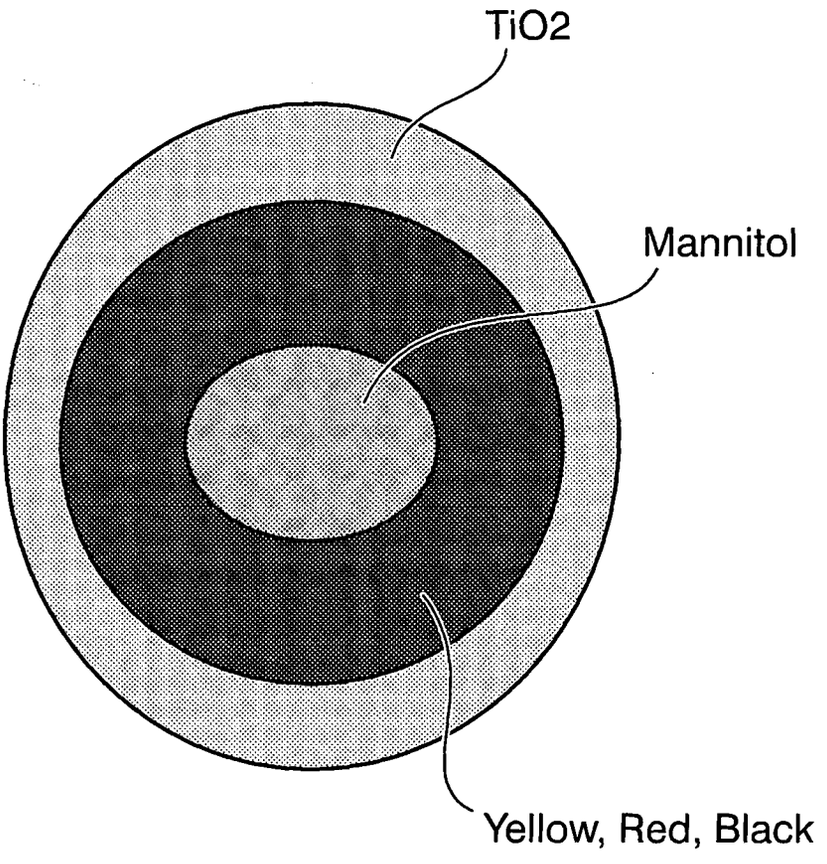


Figure 2

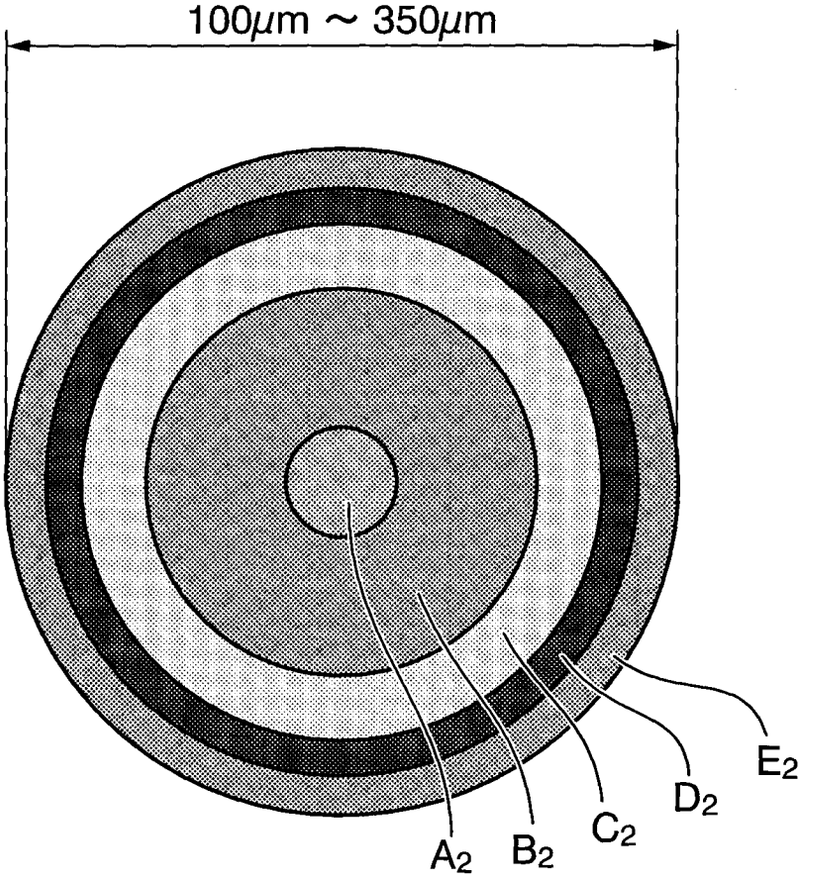


Figure 3

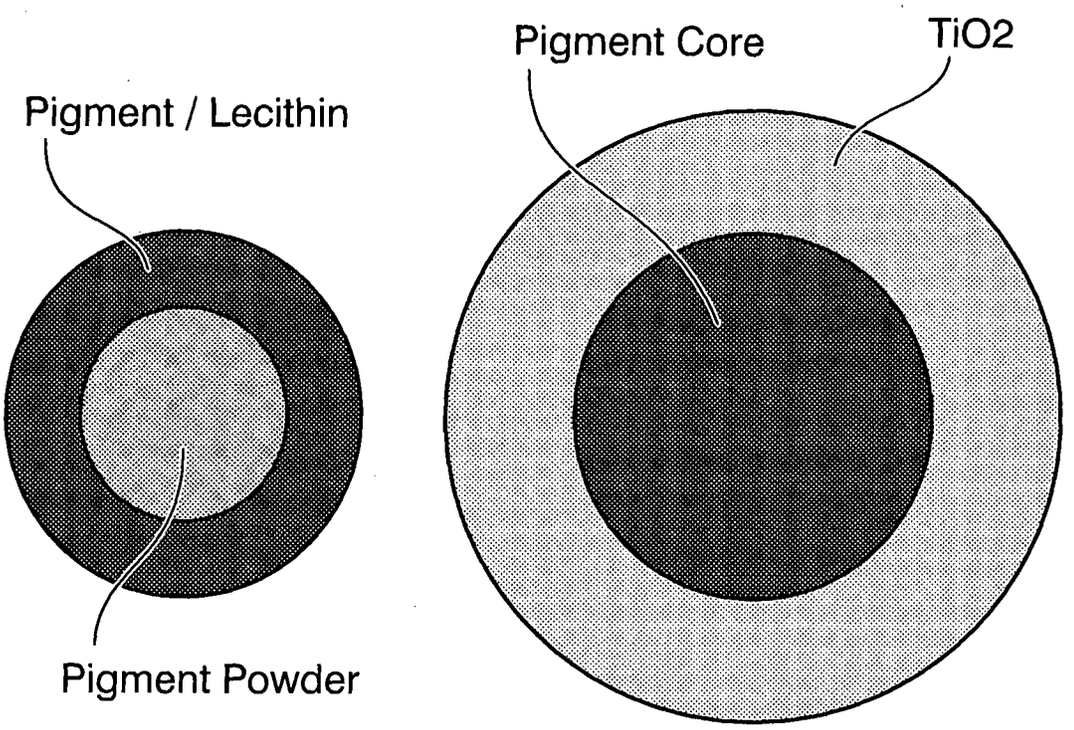


Figure 4

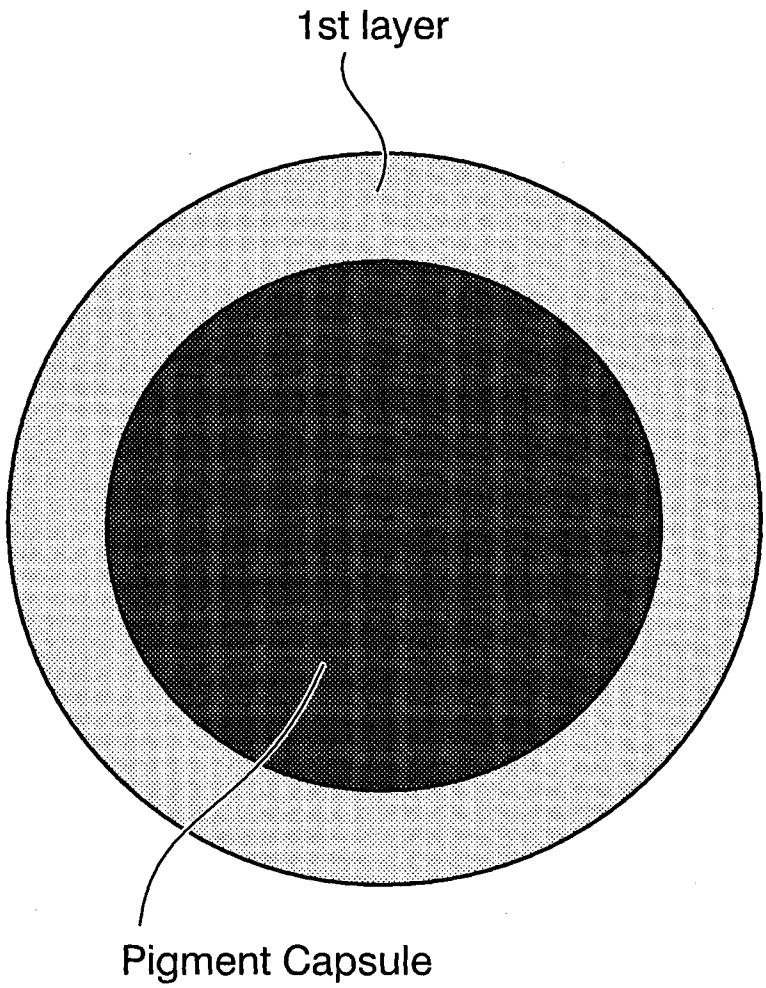


Figure 5

INTERNATIONAL SEARCH REPORT

International application No
PCT/JP2014/084756

A. CLASSIFICATION OF SUBJECT MATTER
INV. A61Q1/02 A61K8/06 A61K8/11
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
A61Q A61K

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2011/229536 A1 (KVITNITSKY EMMA [IL] ET AL) 22 September 2011 (2011-09-22) claims; examples	1-22
X	WO 2013/107354 A1 (OREAL [FR]; CHAI YIHAO [CN]) 25 July 2013 (2013-07-25) claims; example 1	1-4,6-22
A	EP 2 474 299 A2 (BIOGENICS INC [KR]) 11 July 2012 (2012-07-11) the whole document	1-22

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

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

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
16 March 2015	23/03/2015

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Donovan-Beermann, T

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	SHINODA ET AL: "The Stability of O/W type emulsions as functions of temperature and the HLB of emulsifiers: The emulsification by PIT-method", JOURNAL OF COLLOID AND INTERFACE SCIENCE, ACADEMIC PRESS, NEW YORK, NY, US, vol. 30, no. 2, 1 June 1969 (1969-06-01), pages 258-263, XP022505820, ISSN: 0021-9797, DOI: 10.1016/S0021-9797(69)80012-3 cited in the application the whole document -----	1-22
A	MITSUI T ET AL: "APPLICATION OF THE PHASE-INVERSION-TEMPERATURE METHOD TO THE EMULSIFICATION OF COSMETICS", AMERICAN PERFUMER AND COSMETICS, ALLURED PUB., OAK PARK, IL, US, vol. 87, no. 12, 1 December 1972 (1972-12-01), pages 33-36, XP008034619, ISSN: 0003-0392 cited in the application the whole document -----	1-22
X,P	EP 2 774 597 A1 (ORÉAL L [FR]) 10 September 2014 (2014-09-10) claims; examples -----	1-4,6-22
E	EP 2 823 804 A1 (ORÉAL L [FR]) 14 January 2015 (2015-01-14) claims; example 2 -----	1-4,6-22

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/JP2014/084756

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2011229536 A1	22-09-2011	CN 102088946 A	08-06-2011
		EP 2293761 A2	16-03-2011
		JP 2011519969 A	14-07-2011
		KR 20110021853 A	04-03-2011
		US 2011229536 A1	22-09-2011
		WO 2009138978 A2	19-11-2009
WO 2013107354 A1	25-07-2013	EP 2804672 A1	26-11-2014
		JP 2015503599 A	02-02-2015
		KR 20140113727 A	24-09-2014
		US 2014341987 A1	20-11-2014
		WO 2013106998 A1	25-07-2013
		WO 2013107354 A1	25-07-2013
EP 2474299 A2	11-07-2012	EP 2474299 A2	11-07-2012
		JP 2011529104 A	01-12-2011
		KR 100978583 B1	27-08-2010
		US 2011165208 A1	07-07-2011
		WO 2011027960 A2	10-03-2011
EP 2774597 A1	10-09-2014	EP 2774597 A1	10-09-2014
		WO 2014136061 A2	12-09-2014
EP 2823804 A1	14-01-2015	EP 2823804 A1	14-01-2015
		WO 2015004629 A1	15-01-2015