(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
9 April 2009 (09.04.2009)

PCT

(10) International Publication Number
WO 2009/044363 A2

(51) International Patent Classification:
A61K 8/02 (2006.01) *A61K 8/49* (2006.01)
A61Q 19/00 (2006.01)

(21) International Application Number:
PCT/IB2008/054033

(22) International Filing Date: 2 October 2008 (02.10.2008)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
0758017 2 October 2007 (02.10.2007) FR
60/960,739 11 October 2007 (11.10.2007) US

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

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

Published:
— *without international search report and to be republished upon receipt of that report*

WO 2009/044363 A2

(54) Title: A COMPOSITION FOR APPLYING TO KERATINOUS MATERIALS, THE COMPOSITION INCLUDING A HOLOGRAPHIC PIGMENT

(57) Abstract: The present invention provides a composition for applying to keratinous materials, the composition comprising, in a medium that is acceptable for keratinous materials, at least one holographic pigment that is sensitive to a stimulus.

A COMPOSITION FOR APPLYING TO KERATINOUS MATERIALS, THE COMPOSITION INCLUDING A HOLOGRAPHIC PIGMENT

The present invention relates to compositions for applying to keratinous materials and to makeup or treatment methods that include applying such compositions to keratinous materials.

US 4 898 192 discloses an artificial nail including a hologram.

FR 2 798 286 and FR 2 816 508 disclose a make up composition comprising a matrix arranged to confer an holographic effect to the composition.

US 2007/0032846 discloses a holographic tattoo based on a holographic pattern.

Cosmetic or dermatological compositions are frequently applied to the skin of people having a skin that is colored or that presents pigmented marks, rosacea, or wrinkles, the compositions serving to lighten the complexion and/or make it uniform.

Those compositions may include agents for whitening the skin.

It may be necessary to use such whitening agents in prolonged manner and in high quantities in order to observe an effect. The effect resulting from applying such compositions is not necessarily immediate.

Those compositions may also include fluorescent compounds, in particular optical brighteners. Such compositions provide an immediate lightening effect only under predefined lightening conditions, e.g. high intensity natural light.

Compositions including covering substances for hiding skin imperfections are also known. Nevertheless, such compositions can mask the natural appearance of the skin and give the user the sensation of wearing a mask.

Compositions including interference pigments arranged to hide skin imperfections also exist. Nevertheless, such interference pigments can give the skin a shiny and unnatural appearance.

There exists a need to benefit from a composition that presents an effect of lightening and/or making more uniform the complexion, while preserving as much as possible the natural appearance of the skin.

Finally, interference pigments presenting a surface diffraction grating are also known. Such pigments are used, for example, to extend the color path of a makeup composition.

There exists a need to benefit from novel compositions for applying to keratinous materials that are capable, for example, of producing novel optical effects after application and/or while in use.

The invention seeks to satisfy all or some of the above-mentioned needs.

Exemplary embodiments of the invention provide a composition for applying to keratinous materials, the composition comprising, in a medium that is acceptable for keratinous materials, at least one holographic pigment that is sensitive to a stimulus, e.g. a holographic pigment comprising a polymer matrix, e.g. a polymer matrix in which a volume hologram is recorded.

The invention provides new possibilities in terms of optical effects by using such a holographic pigment, which pigment can be sensitive to its environment, thus enabling the appearance of the composition to vary, in particular to vary in a manner that can be seen by the naked eye under the conditions of use of the composition.

The stimulus is different from an optical stimulus.

The stimulus may be constituted by the content of at least one compound in the environment of the pigment. The compound may be at least one of the ingredients of the composition, e.g. a solvent of the composition or an analyte present in and/or on the keratinous materials.

By way of example, the invention may make it possible to provide a composition that changes appearance on application, thus making it possible, for example, to encourage the use of the composition and/or to create an

entertaining effect and/or an appearance effect that is attractive for the user.

By way of example, the polymer matrix may be hydratable, and the optical properties of the hologram may depend on the hydration state of the matrix. This may enable the composition to change appearance on drying. For example, the pigment may be colorless in the composition prior to application and may develop at least one color on application.

With a care product, the fact that the pigment is colorless prior to application may encourage the user to use the composition since it is colorless, in preference to a composition that appears colored prior to application.

Other exemplary embodiments of the invention provide a method of cosmetic or dermatological treatment comprising applying a composition as defined above to keratinous materials.

The composition including the holographic pigment of the invention may also be used, where appropriate, in association with another composition for applying to keratinous materials, either as a base coat or as a top coat.

Holographic pigment

The holographic pigment of the invention may comprise a polymer matrix in which a volume hologram is recorded.

A volume hologram differs from a surface hologram obtained by embossing or etching. By way of example, the matrix may present internally a periodic variation in refractive index and/or in the concentration of an absorbent material.

By way of example, a particle of holographic pigment may comprise a polymer matrix having a volume hologram recorded therein in the form of a series of fringes, e.g. grains that result from developing the hologram, e.g.

grains of silver, leading to periodic variation in the refractive index of the matrix.

The volume hologram converts incident light into one or more beams having spatial and spectral dependencies that are function of the parameters of the hologram.

An example of a volume hologram is a hologram of the "Denisyuk" type, which is reflection hologram that can be obtained in a holographic film with the help of a single laser beam, the beam serving both as the object beam and as the reference beam, as disclosed in application EP 1 754 968 A2 and on the web site http://www.smartholograms.com/site/sections/technology/creating-sensors.htm, and in application EP 1 369 681 A1 (see Figures 1a and 1b in particular), these publications being incorporated by reference.

In order to fabricate the holographic film, a polymer that is soluble in a solvent that is itself compatible with silver and with halogenated salts of silver may be selected, usually water, the polymer also being selected to stabilize the growth of the colloidal particles of silver halide, and to be capable of forming a film that is stable and that becomes insoluble in the conditions required for working the film.

As recalled in WO 99/63408, a known holographic film is a film of a polymer such as gelatin, for example, containing silver halides that are obtained by forming a colloidal liquid phase and depositing it on a suitable support.

Publication WO 99/63408 discloses examples of methods that enable a holographic film to be made with polymers other than gelatin.

A modification of the polymer matrix in the composition of the invention may lead to an alteration of the optical properties of the hologram, in particular to a modification in the wavelength that is reflected, which may lead to a change in the color of the pigment.

Thus, the optical response of the pigment to the stimulus may be a variation in color or in color intensity.

The polymer matrix may be configured in such a manner as to respond to one or more stimuli that lead to modification of the volume hologram.

As mentioned above, an example of such a stimulus, lies in modifying the content of a compound in the environment of the pigment, thereby leading to a modification of the polymer matrix, e.g. to the matrix expanding or shrinking.

By way of example, the pigment may pass, on drying, from a wet environment, e.g. hydrated, in which the matrix is expanded, to a dry environment, e.g. anhydrous, where the matrix is shrunk, as the composition dries.

The polymer matrix may be arranged in such a manner that the pigment is colorless in the composition prior to application, and becomes colored as it dries, e.g. because of the evaporation of a volatile solvent, e.g. water, or on the contrary it may go from being colored to colorless, or else it may change color.

The polymer matrix may also be selected in such a manner as to react chemically with certain analytes such as for example: sebum; contents of metallic ions, of heavy metals, of sulfides, of carbonate/bicarbonate, of alcohol; to enzymes; to a content of glucose, of lactose/glutamate, of β-lactose, of urea, of amylase, or protease, of oxydase, and of certain gases (e.g. O_2, CO_2, NO, NH_3).

The polymer matrix may be subjected to a modification that may be reversible or non-reversible, such that the appearance of color or the change of color is reversible or non-reversible.

For example, the holographic pigment color may disappear on the polymer matrix being re-wetted, in particular re-hydrated.

The appearance of color due to the holographic pigment may also be transient, which may serve for example to allow various colors to appear in succession, e.g. as a function of the extent to which the composition has dried or as a function of the quantity of a predefined analyte on the surface of the keratinous materials.

A transient appearance is obtained, for example, when the environment of the pigment varies between extreme states and the pigment changes appearance twice between those extreme states.

For example, the pigment may be colorless in one of its extreme states, become colored, and then become colorless again in the other extreme state. By way of example, the holographic pigment may reflect a range of wavelengths in the visible while in its intermediate state, and it may reflect ranges of wavelengths that are situated respectively in the infrared and in the ultraviolet when it is in the above-mentioned extreme states.

The holographic pigment may be produced in various ways.

The pigments may be obtained by grinding a macroscopic volume-holograph film, e.g. obtained as described above, the pigment then presenting, by way of example, a mean volume size lying in the range 5 micrometers (μm) to 500 μm.

The holographic film may be ground with conventional grinder means, such as for example a ball grinder, an airjet knife, or by cryogrinding. The holographic film may also be fragmented by pulverization.

WO 2004/103345, incorporated by reference, discloses examples of grinder means.

By way of example, the polymer matrix may comprise at least one natural or synthetic polymer, which may be a homopolymer or a copolymer.

The polymer matrix may comprise a polymer presenting a structure that is regular, e.g. having at least 50 to 100 repetition units in the primary chain.

The polymer matrix may include at least one polymer selected from: polyvinyl alcohol; polyvinyl pyrrolidone; polyhydroxyethyl acrylate; polyhydroxethyl methacrylate; polyacryl amide; polymethacryl amide; and polymers with lower critical solution temperature (LCST) grafts such as those disclosed in US 7 115 225, US 6 689 856, WO 02/055589, and WO 02/055607, and those of natural origin such as gelatin, agarose, and cellulose derivatives, this list not being limiting.

The polymer matrix may comprise a gel, in particular a hydratable gel.

An example of a holographic film that reacts to hydration state is described in paragraph [0095] of application EP 1 754 968 A2, incorporated by reference. In that example, the hologram is recorded in a polymer matrix of gelatin formed by a technique such as that disclosed by H. Thiry in Journal of Photographic Science, Vol. 35, 1987.

The content by weight of holographic pigment in the composition may lie in the range 0.01% to 10%, preferably in the range 0.5% to 5%, better in the range 0.5% to 3%, relative to the total weight to the composition.

The composition may include two holographic pigments of exemplary embodiments of the invention that are different so as to produce different colors in response to the same stimulus, and/or so as to react respectively to different stimuli.

Naturally, the invention is not limited to the particular way in which the volume hologram is made.

Acceptable medium

The composition includes a medium that is compatible with application thereof on external keratinous materials.

The composition may thus include a cosmetically or dermatologically acceptable medium, i.e. a medium that is not toxic and that is suitable for application to the skin, to the integuments, in particular to hair, nails, and eyelashes, or to the lips of human beings.

The acceptable medium is generally adapted to the nature of the support on which the composition is to be applied and also to the form in which the composition is packaged.

The composition may include at least one coloring agent other than the holographic pigment, at a content that does not impede the desired effect.

Other coloring agents

The coloring agent may be an optionally-particulate compound.

The composition may include at least one coloring agent that produces light by absorbing at least a portion of the visible spectrum.

Such a coloring agent that produces a color by an absorption phenomenon may be constituted by a pigment that is organic, or inorganic, or hybrid, comprising both organic material and inorganic material. The composition may comprise a composite pigment, comprising a core coated at least in part by a husk.

The composition may include at least one coloring agent that produces substantially the same color as the holographic pigment in a predefined state thereof. By way of example, this may make it possible to reinforce the color in response to stimulus, e.g. when the composition dries.

When the coloring agent includes a colorant, it may be selected from liposoluble and hydrosoluble colorants.

By way of example, liposoluble colorants are Sudan Red, DC Red 17, DC Green 6, β-carotene, soy oil, Sudan brown, DC Yellow 11, DC Violet 2, DC orange 5, quinoline yellow.

By way of example, hydrosoluble colorants are beetroot juice and methylene blue.

The coloring agent may also be a lake or an organic pigment selected from the following materials and mixtures thereof:

· cochenille carmine;

· organic pigments of the following dyes: azo; anthraquinoid; indigoid; xanthenic; pyrenic; quinolinic; triphenylmethane; fluorane; and

· organic lakes or insoluble salts of sodium, potassium, calcium, barium, aluminum, zirconium, strontium, titanium, acid dyes such as the following dyes: azo; anthraquinoid; indigoid; xanthenic; pyrenic; quinolinic; triphenylmethane; fluorane, which dyes may include at least one carboxylic or sulfonic acid group.

Amongst organic pigments, particular mention may be made of those known under the following names: 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, FD&C Yellow No. 6.

The coloring agent may be an organic lake supported by an organic support such as colophane or aluminum benzoate, for example.

Amongst organic lakes, mention may be made in particular of those known under the following names: D&C Red No. 2 Aluminium lake, D&C Red No. 3 Aluminium lake, D&C Red No. 4 Aluminium lake, D&C Red No. 6 Aluminium 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. 7 Aluminium 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 Aluminium 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 Aluminium lake, D&C Red No. 19 Barium lake, D&C Red No. 19 Zirconium lake, D&C Red No. 21 Aluminium lake, D&C Red No. 21 Zirconium lake, D&C Red No. 22 Aluminium lake, D&C Red No. 27 Aluminium lake, D&C Red No. 27 Aluminium/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 Aluminium lake, D&C Red No. 30 lake, D&C Red No. 31 Calcium lake, D&C Red No. 33 Aluminium lake, D&C Red No. 34 Calcium lake, D&C Red No. 36 lake, D&C Red No. 40 Aluminium lake, D&C Blue No. 1 Aluminium lake, D&C Green No. 3 Aluminium lake, D&C Orange No. 4 Aluminium lake, D&C Orange No. 5 Aluminium lake, D&C Orange No. 5 Zirconium lake, D&C Orange No. 10 Aluminium lake, D&C Orange No. 17 Barium lake, D&C Yellow No. 5 Aluminium lake, D&C Yellow No. 5 Zirconium lake, D&C Yellow No. 6 Aluminium lake, D&C Yellow No. 7 Zirconium lake, D&C Yellow No. 10 Aluminium lake, FD&C Blue No. 1 Aluminium lake, FD&C Red No. 4 Aluminium lake, FD&C Red No. 40 Aluminium lake, FD&C Yellow No. 5 Aluminium lake, FD&C Yellow No. 6 Aluminium lake.

The chemicals corresponding to each of the above-mentioned organic coloring materials are given in the work "International Cosmetic Ingredient Dictionary and Handbook", 1997 edition, pp. 371 to 386 and 524 to 528, published by "The Cosmetic, Toiletry, and Fragrance Association", the content of which is incorporated in the present application by reference.

The composition may contain at least one goniochromatic coloring agent other than the holographic pigment.

By way of example, the goniochromatic coloring agent may be selected from multilayer interference structures and liquid crystal coloring agents.

As the goniochromatic coloring agent, it is possible to use nacres, effect pigments on a synthetic substrate, in particular a substrate of the following types: alumina, silica, borosilicate, iron oxide, aluminum, or interference holographic flakes from a film of polyterephthalate.

The term "nacre" is used to mean colored particles of any shape, optionally iridescent, and in particular those produced by certain mollusks in their shells, or else synthesized, and presenting a color effect by optical interference.

Nacres may be selected from nacreous pigments such as titanium mica covered in an iron oxide, mica covered in bismuth oxychloride, titanium mica covered in chromium oxide, titanium mica covered in an organic dye, in particular of the above-specified type, and also nacreous pigments based on bismuth oxychloride. It is also possible to use particles of mica having at least two successive layers of metallic oxides and/or organic coloring materials superposed on the surface thereof.

The nacres may more particularly possess a color or sheen that is yellow, pink, red, bronze, orangey, brown, and/or coppery.

As an illustration of nacres that may be incorporated in the first composition, mention may be made in particular of gold-colored nacres, in particular those sold by the company Engelhard under the names Brillant gold 212G (Timica), Gold 222C (Cloissone), Sparkle gold (Timica), Gold 4504 (Chromalite), and Monarch gold 233X (Cloissone); bronze nacres, in particular those sold by the supplier Merck under the names Bronze fine (17384) (Colorona) and Bronze (17353) (Colorona), and by Engelhard under the name Super bronze (Cloissone); orange nacres in particular those sold by

Engelhard under the names Orange 363C (Cloissone) and Orange MCR 101 (Cosmica), and by Merck under the names Passion orange (Colorona) and Matte orange (17449) (Microna); the brown-hued nacres sold in particular by Engelhard under the names Nu-antique copper 340XB (Cloissone) and Brown CL4509 (Chromalite); copper sheen nacres, in particular those sold by Engelhard under the name Copper 340A (Timica); red sheen nacres in particular those sold by Merck under the name Sienna fine (17386) (Colorona); yellow sheen nacres, in particular those sold by Engelhard under the name Yellow (4502) (Chromalite); red-hued nacres with a gold sheen, in particular those sold by Engelhard under the name Sunstone G012 (Gemtone); pink nacres, in particular those sold by Engelhard under the name Tan opale G005 (Gemtone); black nacres with gold sheen, in particular those sold by Engelhard under the name Nu antique bronze 240 AB (Timica); blue nacres, in particular as sold by Merck under the name Matte blue (17433) (Microna); white nacres with silver sheen, in particular those sold by Merck under the name Xirona Silver; and golden green pinky orangey nacres, in particular those sold by Merck under the name Indian summer (Xirona), and mixtures thereof.

The nacres may also be those described in EP 1 656 927, having a mean volume size of less than 40 µm, better 15 µm, in particular nacres of the mica/oxide of tin/titanium oxide such as for example those sold under the names TIMIRON SILK BLUE®, TIMIRON SILK RED®, TIMIRON SILK GREEN®, TIMIRON SILK GOLD®, and TIMIRON SUPER SILK® proposed by Merck, and the mica/iron oxide/titanium oxide nacres such as for example FLAMENCO SATIN BLUE®, FLAMENCO SATIN RED®, and FLAMENCO SATIN VIOLET®, proposed by Engelhard, and mixtures thereof.

The composition may also include reflecting particles selected from particles comprising a synthetic substrate coated at least in part in at least one layer of at least one metallic oxide, e.g. selected from the

oxides of titanium, in particular TiO_2, iron, in particular Fe_2O_3, tin, chromium, barium sulfate and the following materials: MgF_2, CrF_3, ZnS, ZnSe, SiO_2, Al_2O_3, MgO, Y_2O_3, SeO_3, SiO, HfO_2, ZrO_2, CeO_2, Nb_2O_5, Ta_2O_5, MoS_2, and mixtures thereof.

As examples of such particles, mention may be made of particles comprising a synthetic mica substrate coated in titanium dioxide, or glass particles coated either in brown iron oxide, titanium oxide, tin oxide, or a mixture thereof, such as those sold under the trademark REFLECKS® by Engelhard.

The composition may also include a coloring agent that is thermochromic, mecanochromic, or photochromic.

The composition may include a solvatochromic coloring agent, e.g. DC Red 7.

Solvents

The composition may include at least one solvent, in particular selected as a function of its galenic form.

It is also possible to select the nature of the solvent so that it interacts or does not interact with the polymer matrix of the holographic pigment.

Selecting a solvent with the ability to interact with the matrix may serve for example to change the optical properties of the hologram as a function of the solvent content in the environment of the pigment, which may serve for example to cause color to appear and/or color to change during drying.

Selecting a solvent that does not interact with the matrix may serve to make the holographic pigment sensitive to a stimulus other than solvent content in the medium surrounding the pigment, and this may make it easier to observe a modification in the hologram in response to the presence of an analyte, e.g. lactic acid, urea, pH, etc.

The composition may comprise water, an aqueous solvent, or a mixture of water and hydrophilic organic

solvents commonly used in cosmetics, such as alcohols, and in particular linear or branching lower monoalcohols having 2 to 5 carbon atoms such as ethanol, isopropanol, or n-propanol, polyols such as glycerin, diglycerin, propylene glycol, sorbitol, pentyl glycol, polyethylene glycols. The first composition may also contain C_2 ethers and C_2-C_4 hydrophilic aldehydes.

The water or the mixture of water and hydrophilic organic solvents may be present in the composition at a content lying for example in the range 0% to 90%, in particular 0.1% to 90% by weight, and preferably 0% to 60% by weight, in particular 0.1% to 60% by weight, relative to the total weight of the composition.

The composition may include a solvent that is volatile, aqueous, or organic.

In the meaning of the present invention, the term "volatile solvent" means a solvent that is liquid at ambient temperature, in particular having a vapor pressure that is not zero at ambient temperature and atmospheric pressure, in particular having a vapor pressure lying in the range 0.13 pascals (Pa) to 40,000 Pa (10^{-3} millimeters of mercury (mmHg) to 300 mmHg), and preferably lying in the range 1.3 Pa to 13,000 Pa (0.01 mmHg to 100 mmHg), and preferably lying in the range 1.3 Pa to 1300 Pa (0.01 mmHg to 10 mmHg).

When the composition includes one or more organic solvents, these solvents may be present at a content lying in the range 0.1% to 99% relative to the total weight of the composition in question.

In general, the quantity of solvent, in particular of organic solvent, depends on the nature of the support onto which the composition is to be applied.

The composition may include at least one volatile solvent constituted by a volatile oil.

The oil may be a silicone oil or a hydrocarbon oil, or it may comprise a mixture of such oils.

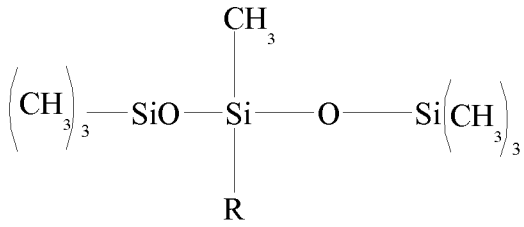
In the meaning of the present invention, the term "silicone oil" is used to mean an oil including at least one silicon atom, and in particular at least one Si-O group.

The term "hydrocarbon oil" is used to mean an oil containing mainly atoms of hydrogen and carbon, and possibly atoms of oxygen, nitrogen, sulfur, and/or phosphorus.

The volatile hydrocarbon oils may be selected from hydrocarbon oils having 8 to 16 atoms of carbon, in particular C_8-C_{16} branching alkanes (also known as isoparaffins), such as isododecane (also known as 2,2,4,4,6-pentamethyl heptane), isodecane, isohexadecane, and for example the oils sold under the trade marks ISOPARS® or PERMETHYLS®.

As volatile oils, it is also possible to use volatile silicone oils, such as for example, volatile linear or cyclic silicon oils, in particular those having viscosity ≤ 8 centistokes (cSt) (8×10^{-6} square meters per second (m^2/s)), and having in particular 2 to 10 atoms of silicon, in particular 2 to 7 atoms of silicon, these silicone oils optionally including alkyl or alkoxy groups having 1 to 10 carbon atoms. As a volatile silicone oil suitable for use in the invention, mention can be made in particular of the following: dimethicones of viscosity 5 cSt to 6 cSt; octamethyl cyclotetrasiloxane; decamethyl cyclopentasiloxane; dodecamethyl cyclohexasiloxane; heptamethyl hexyltrisiloxane; heptamethyloctyl trisiloxane; hexamethyl disiloxane; octamethyl trisiloxane: decamethyl tetrasiloxane; dodecamethyl pentasiloxane; and mixtures thereof.

Mention may also be made of volatile linear alkyltrisiloxane oils having the following general formula (I):



where R represents an alkyl group having 2 to 4 carbon atoms and in which one or more hydrogen atoms may be substituted by an atom of fluorine or of chlorine.

Amongst oils having the general formula (I), mention may be made of the following:

- 3-butyl 1,1,1,3,5,5,5-heptamethyl trisiloxane;
- 3-propyl 1,1,1,3,5,5,5-heptamethyl trisiloxane; and
- 3-ethyl 1,1,1,3,5,5,5-heptamethyl trisiloxane,

corresponding to oils of formula (I) for which R is respectively a butyl group, a propyl group, or an ethyl group.

It is also possible to use fluorinated volatile oils such as nonafluoromethoxy butane or perfluoromethyl cyclopentane, and mixtures thereof.

A composition of the invention may for example include 0.01% to 95% by weight of volatile oil, relative to the total weight of the composition, better 1% to 75% by weight.

The composition may include at least one organic solvent selected from the following list:

- ketones that are liquid at ambient temperature such as methylethyl ketone, methylisobutyl ketone, diisobutyl ketone, isophorone, cyclohexanone, and acetone;
- alcohols that are liquid at ambient temperature such as ethanol, isopropanol, alcohol diaketone, 2-butoxyethanol, and cyclohexanol;
- glycols that are liquid at ambient temperature such as ethylene glycol, propylene glycol, pentylene glycol, and glycerol;

· propylene glycol ethers that are liquid at ambient temperature such as propylene glycol monomethylether, propylene glycol monomethyl ether acetate, and dipropylene glycol mono n-butyl ether;

· short chain esters (having a total of 3 to 8 carbon atoms) such as ethyl acetate, methyl acetate, propyl acetate, n-butyl acetate, and isopentyl acetate;

· alkanes that are liquid at ambient temperature such as decane, heptane, dodecane, and cyclohexane.

Fatty phase

When the composition is for application to the lips or to the eyelashes, it may include a fatty phase, and in particular at least one fatty body that is liquid at ambient temperature (25°C) and atmospheric pressure (760 mmHg), and/or a fatty body that is solid at ambient temperature such as waxes, pasty fatty bodies, gums, and mixtures thereof. The fatty phase may also contain lipophile organic solvents.

By way of example, the composition may present a continuous fatty phase capable of containing at least 5% water, in particular at least 1% water relative to its total weight, and in particular it may be in anhydrous form.

As examples of fatty bodies that are liquid at ambient temperature, often called "oils", mention may be made of the following: vegetable hydrocarbon oils such as liquid triglycerides of fatty acids having 4 to 10 carbon atoms such as triglycerides of heptanoic or octanoic acid, or indeed oils of: sunflower, maize (corn), soybean, grape pips, sesame, apricot, macadamia, casterbean, avocado, triglycerides of caprylic/capric acid, jojoba oil, karite butter, lanolin, acetylated lanolin; linear or branching hydrocarbons of mineral or synthetic origin such as paraffin oils and derivatives thereof, Vaseline, polydecenes, hydrogenated polyisobutene such as parleam; synthetic esters and

ethers, in particular of fatty acids such as, for example Purcellin oil, isopropyl myristate, ethyl-2-hexyl palmitate, octyl-2-dodecyl stearates, octyl-2-dodecyl erucate, isostearyl isostearate; hydroxyl esters such as isostearyl lactate, octylhydroxystearate, octyldodecyl hydroxystearate, diisostearyl malate, triisocetyl citrate, heptanoates, octanoates, fatty acid decanoates; isononyl isonanoate, isopropyl lanolate, tridecyl trimellilate, diisostearyl malate; polyol esters such as propylene glycol dioctanoate, neopentyl glycol diheptanoate, diethylene glycol diisononanoate; and esters of pentaerythritol; fatty acids having 12 to 26 carbon atoms such as octyldodecanol, 2-butyloctanol, 2-hexyldecanol, 2-undecylpentadecanol, olecic alcohol; partially hydrocarbon and/or silicone fluorinated oils; silicone oils such as optionally volatile polymethylsiloxanes (PDMS) that are linear or cyclic, liquid or pasty at ambient temperature such as cyclomethicones, dimethicones, optionally including a phenyl group, such as phenyl trimethicones, phenyltrimethyl siloxydiphenyl siloxanes, diphenylmethyl dimethyl trisiloxanes, diphenyl dimethicones, phenyl dimethicones, polymethylphenyl siloxanes; and mixtures thereof. The oils may present a content lying in the range 0.01% to 90%, and that are 0.1% to 85% by weight, relative to the total weight of the composition.

The presence of an oily phase may impart shine, and the oily phase may for example present a refractive index lying in the range 1.47 to 1.51, better in the range 1.48 to 1.50. The refractive index is measured at ambient temperature (25°C) using a refractometer.

The composition may include at least one agent for structuring the liquid fatty phase (formed by the above-described volatile or non-volatile organic solvents and/or oils) selected from waxes, semicrystalline polymers, lipophil gelling agents, and mixtures thereof.

The pasty fatty bodies are generally hydrocarbon compounds with a melting point lying in the range 25°C to 60°C, for example in the range 30°C to 45°C, and/or with hardness lying in the range 0.001 megapascals (MPa) to 0.5 MPa, in particular in the range 0.005 MPa to 0.4 MPa, such as lanolins and derivatives thereof.

The waxes may be solid at ambient temperature (25°C), changing reversibly between the solid and liquid state, having a melting temperature higher than 30°C and possibly as high as 200°C, hardness greater than 0.5 MPa, and presenting in the solid state a crystal organization that is anisotropic. In particular, the waxes may present a melting temperature higher than 25°C, and better higher than 45°C. The waxes may be hydrocarbon waxes, fluorinated waxes, and/or silicone waxes, and they may be of vegetable, mineral, animal, and/or synthetic origin. As waxes that are suitable, mention may be made of beeswax, Carnauba or Candellila wax, paraffin, microcrystalline waxes, ceresin wax or ozokerite wax; synthetic waxes such as polyethylene waxes or Fischer-Tropsch waxes, silicone waxes such as alkyl or alkoxy-dimethicone having 16 to 45 carbon atoms. The composition may contain 0 to 50% by weight of waxes, relative to the total weight of the composition, better 1% to 30% by weight.

Gums that are suitable for use are generally polydimethylsiloxanes (PDMS) having high molecular weight or cellulose or polysaccharide gums.

Film-forming polymers

By way of example, the composition may also include a film-forming polymer, in particular for a mascara, a nail varnish, or a foundation. The term "film-forming polymer" is used to designate a polymer suitable on its own or in the presence of an auxiliary film-forming agent, for forming a continuous film that adheres to a support, in particular to a keratinous material. The

composition may also include an auxiliary film-forming agent that encourages the formation of a film with the film-forming polymer.

Amongst the film-forming polymers that are suitable for use in the composition of the invention, mention may be made of synthetic polymers of the radical type or the polycondensate type, polymers of natural origin, such as nitrocellulose or cellulose esters, and mixtures thereof.

The radical type film-forming polymers may in particular be vinyl polymers or copolymers, in particular acrylic polymers.

Vinyl film-forming polymers may result from polymerizing ethylenically unsaturated monomers including at least one acid group and/or esters of such acid monomers and/or amides of such acid monomers, such as α,β-ethylenically unsaturated carboxylic acids such as acrylic acid, methacrylic acid, crotonic acid, maleic acid, itaconic acid.

Vinyl film-forming polymers may also be obtained by homopolymerization or copolymerization of monomers selected from vinyl esters such as vinyl acetate, vinyl neodecanoate, vinyl pivalate, vinyl benzoate, and vinyl t-butyl benzoate, and styrene monomers such as styrene and alpha-methyl styrene.

As film-forming polycondensates, mention may be made of polyurethanes, polyesters, amide polyesters, polyamides, and polyureas, this list not being limiting.

The polymers of natural origin, possibly modified, may be selected from shellac resin, sandarac gum, dammars, elemis, copals, cellulose polymers, such as nitrocellulose, ethylcellulose, or nitrocellulose esters selected, for example, from cellulose acetate, cellulose acetobutyrate, cellulose acetopropionate, and mixtures thereof.

The film-forming polymer may be present in the form of solid particles in an aqueous or oily dispersion, also known as a latex or a pseudolatex. The film-forming

polymer may include one or more stable dispersions of generally spherical polymer particles comprising one or more polymers in a physiologically acceptable liquid fatty phase. These dispersions are generally referred to as non-aqueous dispersions (NAD) of polymer as contrasted with latexes, which are aqueous dispersions of polymer. These dispersions may in particular be in the form of nanoparticles of polymers in stable dispersion in said fatty phase. The nanoparticles preferably have a size lying in the range 5 nanometers (nm) to 600 nm. Techniques for preparing these dispersions are well known to the person skilled in the art.

As an aqueous dispersion of film-forming polymer, it is possible to use the acrylic dispersions sold under the names NEOCRYL XK-90®, NEOCRYL A-1070®, NEOCRYL A-1090®, NEOCRYL BT-62®,' NEOCRYL A-1079®, NEOCRYL A-523® by the company AVECIA-NEORESINS, DOW LATEX 432® by the company DOW CHEMICAL, DAITOSOL 5000 AD® by the company DAITO KASEI KOGYO; or indeed the aqueous dispersions of polyurethane sold under the names NEOREZ R-981®, NEOREZ R-974® by the company AVECIA-NEORESINS, AVALURE UR-405®, AVALURE UR-410®, AVALURE UR-425®, AVALURE UR-450®, SANCURE 875®, SANCURE 861®, SANCURE 878®, SANCURE 2060® by the company GOODRICH, IMPRANIL 85® by the company BAYER, AQUAMERE H-1511® by the company HYDROMER; sulfopolyesters sold under the trade name Eastman AQ by the company Eastman Chemical Products.

The composition may include at least one film-forming polymer that is a film-forming linear sequenced ethylene polymer. The polymer includes for example at least a first sequence and at least a second sequence having different glass transition temperatures (Tg), said first and second sequences being interconnected by an intermediate sequence having at least one monomer constituting the first sequence and at least one monomer constituting the second sequence. The first and second sequences and the sequenced polymer are for example

mutually incompatible. By way of example, such polymers are described in document EP 1 411 069 or WO 04/028488, which are incorporated by reference.

The composition may include at least one filler, in an amount that does not impede the looked-for effect.

Fillers

The term "filler" is used to designate particles of any kind that are insoluble in the medium of the composition, regardless of the temperature at which the composition is fabricated.

A filler may serve in particular to modify the rheology or the texture of the composition. The nature and the quantity of the particles may depend on looked-for textures and mechanical properties.

Examples of fillers that may be mentioned amongst others are the following: talc, mica, silica, kaolin, sericite, powders of polyamide, polyolefin, e.g. polyethylene, polytetrafluoroethylene, polymethyl methacrylate, polyurethane, powders of starch and beads of silicone resin, portions of hollow spheres made of an organosilicone material, with a mean diameter lying in the range 0.05 µm to 10 µm, such as those described in EP 1 530 961, e.g. those commercially available from the company Takemoto Oil & Fat under the trade names NLK-500, NLK-501, and NKL-506.

The fillers may be intended, amongst other things, to create a fuzzy effect, in particular with a foundation, in order to hide imperfections of the skin.

Active agents

The composition may include at least one cosmetically or dermatologically active agent.

As cosmetically, dermatologically, hygienically, or pharmaceutically active agents that are suitable for use in compositions of the invention, mention may be made of the following: hydrating agents, polyols, such as

glycerin for example, vitamins, in particular vitamins C, A, E, F, B, B3, B5, K1, or PP, vitamin derivatives, and in particular their esters, essential fatty acids, essential oils, ceramides, sphingolipids, sun filters that are liposoluble or in the form of nanoparticles, specific agents for treating the skin (protective agents, antibacterial agents, antiwrinkle agents, ...), self-tanning agents, agents that have an effect on the skin, in particular keratolytic agents or agents encouraging peeling, in particular selected from α-hydroxy-acids, β-hydroxy-acids, α-keto-acids, β-keto-acids, retinoids, and esters thereof, retinal, retinoic acid and derivatives thereof, C glycosides and derivatives thereof, adenosine and derivatives thereof, free antiradical agents, DHEA and derivatives thereof, the Q10 coenzyme, whitening and depigmenting agents such as kojic acid, para-aminophenol derivatives, arbutine and derivatives thereof, and mixtures thereof.

Each active agent may be used for example at a concentration lying in the range 0% to 20%, and in particular 0.001% to 15% relative to the total weight of the composition.

The composition may also contain other ingredients commonly used in cosmetics, such as, for example: thickeners, tightening agents, wetting agents, oligo-elements, moisturizers, in particular polyols, e.g. glycerin, softeners, sequestering agents, fragrances, preservatives, antioxidants, pH adjusters (acidic or basic), physical or chemical ultraviolet (UV) filters, and mixtures thereof.

Depending on the intended type of application, a composition of exemplary embodiments of the invention may include any of the ingredients conventionally used in the field under consideration, present in quantities that are appropriate for the desired galenic form.

Galenic forms

The composition may be presented in a variety of forms, depending on its purpose.

The composition may thus be in any of the galenic forms normally used for topical application, and in particular it may be in anhydrous form, in the form of an oily or aqueous solution, a powder that may be free or compacted, a stick, a serum (a thickened aqueous solution), an oily or aqueous gel, an oil-in-water, water-in-oil, wax-in-water, or water-in-wax emulsion, a multiple emulsion, or a dispersion of oil in water by means of vesicles situated at the oil/water interface.

Proposed examples

(quantities expressed in grams (g)

Example 1: care cream (oil-in-water emulsion)

A):

Glyceryl stearate (and) PEG-100 stearate:	2.00 g
Dimyristyl tartrate (and) cetearyl alcohol (and) C12-5 pareth-7 (and) PPG-25 laureth-25:	1.50 g
Cyclohexasiloxane:	10.00 g
Stearyl alcohol:	1.00 g

B):

Water:	80.75 g
Phenoxyethanol:	1.00 g
Pentasodium ethylene diamine tetramethylene phosphate:	0.05 g
Ammonium polyacryldimethyl tauramide:	0.40 g
Xanthan gum:	0.20 g

C):

Holographic pigment of the invention*:	3.00 g

*Pigment obtained by grinding a gelatin-based holographic film.

Method of operation

· Heat phase B to about 75°C and incorporate the ammonium polyacryldimethyl tauramide therein; stir until a homogenous gel is obtained.

· Heat phase A to about 75°C.

· Make the emulsion by incorporating phase A in phase B.

· At 40°C-45°C incorporate phase C and continue stirring until cooling is complete.

The effect obtained may be viewed as follows.

The composition is spread at 30 µm on the black portion of an Erichsen type 24/5 contrast card using an automatic applicator from Braive Instruments.

The spread composition is then placed in a stove that is ventilated and thermostatically set at 37°C for a period of 24 hours.

The color associated with the change in the state of the holographic particles may be seen by the naked eye.

It is also possible to measure the L, a, and b parameters of the dry film and the L, a, and b parameters of the wet film using a Minolta CR400 colorimeter. The color difference ΔE ($\Delta E = [(\Delta a)^2 + (\Delta b)^2 + (\Delta L)^2]^{0.5}$) between these two states of the film is greater than 1.

Example 2: foundation (water in oil emulsion)

A):

Polymethylcetyl dimethyl methylsiloxane oxyethylene	1.5 g
Polyglycerole isotearate	0.5 g
Dimethicone	2.05 g
Cyclopentasiloxane	4.00 g
Red iron oxide sold under the reference BRO-12 by the company Kobo	0.76 g
Yellow iron oxide sold under the reference BYO-12 by Kobo	1.59 g
Black iron oxide sold under the reference BBO-12 by Kobo	0.31 g
Titanium dioxide sold under the reference BTD-401	

by Kobo	10.68 g
Isonoyl isononanoate	6.66 g
Preservative	0.15 g

B):

Water	qsp
Propylene glycol	3.00 g
Magnesium sulfate	1.75 g
Methylparaben	0.2 g
Preservative	0.3 g

C):

Nylon® 12	3.00 g

D):

Holographic pigment of the invention**	5.00 g

**Same pigment as in Example 1.

Method of operation

· Homogenize phase A and phase B separately at ambient temperature while stirring.

· Make the emulsion by incorporating phase B in phase A.

· Incorporate phases C and D while stirring.

The effect obtained may be viewed as follows.

The composition is spread at 30 µm on the black portion of an Erichsen type 24/5 contrast card using an automatic applicator from Braive Instruments.

The spread composition is then placed in a stove that is ventilated and thermostatically set at 37°C for a period of 24 hours.

The color associated with the change in the state of the holographic particles may be seen by the naked eye.

It is also possible to measure the L, a, and b parameters of the dry film and the L, a, and b parameters of the wet film using a Minolta CR400 colorimeter. The

color difference ΔE between these two states of the film is greater than 1.

The term "comprising a" should be understood as being synchronous with "comprising at least one".

CLAIMS

1. A composition for applying to keratinous materials, the composition comprising, in a medium that is acceptable for keratinous materials, at least one holographic pigment that is sensitive to a stimulus.

2. A composition according to claim 1, the holographic pigment comprising a polymer matrix.

3. A composition according to claim 2, in which one volume hologram is recorded in the polymer matrix.

4. A composition according to any one of claims 1 to 3, the stimulus being the content of at least one compound in the environment of the pigment.

5. A composition according to claim 3, the compound being at least one of the ingredients of the composition, in particular a solvent of the composition.

6. A composition according to claim 4, the compound being an analyte present in and/or on the keratinous materials.

7. A composition according to any preceding claim, the pigment having a mean size lying in the range 5 μm to 500 μm.

8. A composition according to any preceding claim, the pigment being arranged, in at least one state that is encountered in the composition prior to application or on application, to reflect wavelengths lying in the range 280 nm to 900 nm.

9. A composition according to claim 2, the polymer matrix being hydratable and the optical properties of the hologram depending on the hydration state of the matrix.

10. A composition according to any one of claims 1 to 9, the holographic pigment being colorless in the composition prior to application thereof, and developing a color on application.

11. A composition according to claim 2, the polymer matrix comprising at least one synthetic polymer.

12. A composition according to claim 11, the polymer matrix comprising at least one polymer selected from: polyvinyl alcohol, polyvinyl pyrrolidone, polyhydroxyethyl acrylate, polyhydroxyethyl methacrylate, polyacryl amide, polymethacryl amide, and polymers with LCST grafts.

13. A composition according to any one of claims 1 to 11, the composition including at least one polymer selected from: gelatin, agarose, and cellulose derivatives.

14. A composition according to any preceding claim, the content by weight of the holographic pigment lying in the range 0.01% to 10%.

15. A composition according to claim 14, the content lying in the range 0.5% to 5%.

16. A composition according to claim 14, the content lying in the range 0.5% to 3%.

17. A composition according to claim 2, the polymer matrix comprising a polymer presenting a regular structure with at least 50 to 100 repetition units in the primary chain.

18. A composition according to claim 2, the polymer matrix being selected in such a manner as to react chemically with analytes such as sebum, to content of

metallic ions, of heavy metals, of sulfides, of carbonate/bicarbonate, of alcohol, of enzymes, of glucose, lactose/glutamate, β-lactose, urea, amylase, protease, oxydase, to certain gases (O_2, CO_2, NO, NH_3), to pH, to lactic acid.

19. A composition according to any one of claims 1 to 18, the acceptable medium comprising water.

20. A composition according to claim 19, the content by weight of water lying in the range 0.5% to 99%.

21. A composition according to any one of claims 1 to 20, having no coloring agent other than the holographic pigment.

22. A composition according to any one of claims 1 to 20, including at least one other coloring agent.

23. A composition according to any preceding claim, including at least one cosmetically or dermatologically active agent.

24. A composition according to any preceding claim, the stimulus being different from an optical stimulus.

25. A cosmetic treatment method comprising applying on keratinous materials a composition according to any preceding claim.