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**(54) Title:** COSMETIC COMPOSITION CONTAINING NITROGEN MONOXIDE IN A MICROPOROUS CRYSTALLINE SOLID MATERIAL

**(57) Abstract:** The invention relates to an anhydrous cosmetic composition containing nitrogen monoxide adsorbed into a microporous crystalline solid material. This composition may be a makeup or care composition for keratin materials, for instance the lips, the eyelashes, the nails or the skin, and may be in the form of a stick, especially of lipstick or of lip balm.

# COSMETIC COMPOSITION CONTAINING NITROGEN MONOXIDE IN A MICROPOROUS CRYSTALLINE SOLID MATERIAL

The present invention relates to a cosmetic composition containing nitrogen monoxide adsorbed by a porous crystalline solid material, and to a dyestuff. This composition is intended to be applied to human keratin materials, for instance the skin, the lips, the eyelashes, the eyebrows, the nails or the hair.

The composition is more particularly intended to be applied to the skin or the lips.

The composition of the invention may consist in particular of a makeup product for the human body, lips or integuments, which may in particular have non-therapeutic care and/or treatment properties. The composition of the invention may in particular constitute a product for coating keratin fibres, for instance the eyelashes, the eyebrows and the hair, and more particularly the eyelashes.

The composition according to the invention may be in the form of a mascara, an eyebrow product, an eyeliner or a hair makeup product.

The composition may be a loose or compacted powder, a foundation, a makeup rouge, an eyeshadow, a blusher, a lipstick, a lip balm, a lip gloss, a lip or eye pencil, a mascara, an eyeliner, a nail varnish, an artificial skin tanning product, a hair colouring product or haircare product, or alternatively a body makeup product or skin colouring product.

Patent application WO 05/003032 proposes the use of zeolites as adsorber for nitrogen monoxide and shows that the active agent is released into water and into the blood. The document moreover describes certain known uses of nitrogen monoxide and suggests using nitrogen monoxide adsorbed into zeolites in cosmetics. However, the said document does not envisage combining a pigment with this active agent to modify the makeup and to obtain novel effects.

The inventors have found that novel colouring effects may be obtained by combining standard dyestuffs with nitrogen monoxide adsorbed into zeolites. The natural coloration of keratin materials caused by the release of the nitrogen monoxide modifies the makeup result produced by the dyestuff usually used in cosmetic compositions. This combination also makes it possible to design a novel makeup and to conceive of novel gestures for users.

One subject of the invention is thus a cosmetic composition containing at least one dyestuff and nitrogen monoxide adsorbed into a microporous crystalline solid material.

The composition according to the invention is in particular intended to improve keratin tissues, such as the skin, the hair, the lips, the nails, the eyelashes and the eyebrows.

One subject of the invention is also the cosmetic use of said composition.

An other subject of the invention is the cosmetic use of said composition for making up the skin, the eyelashes, the eyelids, the lips or the nails.

In particular, the composition may be a care and/or makeup composition for the human eyelashes or for the preparation of a care and/or treatment composition for human eyelashes.

The composition is especially intended to make the lips pouty and/or to promote their naturally pinkish colour, to improve the look of the complexion (healthy appearance) and/or to reduce the shadows around the eyes.

The composition may also be used to improve the appearance of the lips or the area around the lips, especially to increase the volume of the lips and/or to model them and/or to make them smoother. The composition may also be used to modify the colour of the lips, to make them pinker or more vivid, or even to obtain a "bitten lip" effect.

In particular, the composition is intended:

- to make the lips pouty, i.e. increase their size, volume and/or thickness and/or give them a more swollen, fleshy look and/or to model them and/or make them smoother and/or stimulate the naturally pinkish colour of the lips;

- to stimulate the naturally pinkish colour of the skin and/or give the skin a natural healthy appearance;
- to homogenize the complexion and/or promote its radiance and/or luminosity and/or reduce the off-colour or waxy complexion effect;
- to reduce the bags and/or lighten the shadows around the eyes and/or make the complexion in the area under the eyes uniform with the rest of the face.

In one embodiment or application, the compositions of the present invention are useful for delaying, minimizing, effacing and/or preventing the signs of ageing of the skin, in particular the visible and/or palpable discontinuities of the texture of the skin associated with ageing, thus providing an improvement in the appearance and/or feel of the skin, for example a smoother, more uniform appearance and/or feel.

The term "signs of ageing of the skin" means the development of discontinuities of texture such as wrinkles, including fine surface lines and deep coarse wrinkles, the lines on the skin, crevices, bumps, large pores, a flaky appearance, crumbling and/or other forms of inequality or roughness of the skin, loss of elasticity of the skin, sagging (including puffiness in the area of the eyes and the cheeks), loss of firmness of the skin, loss of skin tone and loss of recovery of the skin after deformation.

For example, the length, depth and/or other dimensions of the lines and/or wrinkles may be reduced, the apparent diameter of the pores may reduce, or the apparent height of the tissue in the immediate proximity of the opening of the pores may reduce.

The compositions of the present invention may also be used for stabilizing or remodelling hypodermic fat or deeper fat. Stabilizing fat, especially in human beings, is generally associated with the appearance of ageing attributed to fat atrophy and also to fat regression in the skin. The methods and compositions described in the present text may contribute towards preventing the formation of wrinkles and promote an improvement in the appearance of deep wrinkles by supporting the vascularization of the skin.

**Microporous crystalline solid material**

The composition according to the invention contains at least one organic, mineral or hybrid crystalline solid material. The material is solid at atmospheric pressure and at a temperature of about 40°C.

The crystalline solid material is microporous. The pore size is less than or equal to 1 micron, preferably less than or equal to 1000 Angströms, more preferably less than or equal to 50 Angströms and more preferably less than or equal to 30 Angströms.

The pores may form a repeating three-dimensional network capable of trapping nitrogen monoxide or a complex of nitrogen monoxide with at least one organic or mineral cation.

According to one embodiment, the microporous crystalline solid material is a zeolite. The composition of the present invention may contain nitrogen monoxide adsorbed into a zeolite material.

Zeolite materials are a class of aluminosilicate materials that are known and used in various applications, for example ion exchange, gas separation and catalysis (A. Dyer, An Introduction to Zeolite Molecular Sieves, J. Wiley and Sons, 1988).

The zeolites may be of natural origin or prepared synthetically. Zeolites are structures of nanoporous crystalline aluminosilicates consisting of tetrahedra of $AlO_4$ and $SiO_4$ linked together via the oxygen peaks. The assembly of the tetrahedra in space forms polyhedra that delimit a network of one-, two- or three-dimensional channels, cages and cavities in which travel cations to points where they equilibrate the negative charges borne by the $AlO_4$- tetrahedra. The size and arrangement of the tetrahedra differentiate the zeolites.

Zeolites may be represented by the general formula $Al_ySi_{1-y}O_4^{y-}$. For each aluminium atom in the zeolite structure, a negative charge is equilibrated by a cation external to the framework. These cations may be of mineral or organic nature and may be exchanged by using standard ion-exchange processes (M.E. Davis, Ordered porous materials for emerging applications, Nature, 417, 813, 2002).

Zeolites may comprise cations of a transition element as species external to the framework, for example iron, copper or ruthenium, and the nitrogen monoxide forms complexes inside the cavities of the zeolite material.

Cations of other elements, for example sodium and potassium, bind nitrogen monoxide less strongly. A person skilled in the art can use standard ion-exchange processes to introduce the required metal ions into a zeolite structure as cations external to the framework (Plank et al., US patent No. 3 140 249; Preparation, characterization and performance of Fe-ZSM-5 Catalysts, R. Joyner and M. Stockenhuber, J. Phys. Chem. B., 1999, 103, 5963-5976). Using such techniques, it is possible to incorporate mixtures of cations into zeolite structures.

The zeolites may be in dehydrated form.

The amount of nitrogen monoxide charged into the zeolites may be controlled by varying the relative amounts of the cations external to the framework, by controlling their chemical nature and/or the total number of cations present. For example, the number of cations external to the framework present in the zeolite structure may depend on the amount of aluminium present in the framework. More aluminium ions require more cations external to the framework to equilibrate the negative charge.

The chemical nature of the cations external to the framework may also be modified (for example monovalent cations, e.g. $Na^+$ and $Ag^+$, may be exchanged with divalent cations, for example $Fe^{2+}$ and $Cu^{2+}$, or trivalent cations, for example $Ru^{3+}$ and $Fe^{3+}$). Each different cation may have a different affinity for NO and the change of cations present in the zeolite framework may be used to control the release of NO. Such an adjustment of the zeolite composition may affect the kinetics with which the nitrogen monoxide is released. For example, a sodium-charged zeolite may bind nitrogen monoxide less strongly than an iron-charged zeolite and release nitrogen monoxide more quickly. A sodium/iron mixed zeolite may release nitrogen monoxide at a rate different to that of a sodium-charged zeolite or an iron-charged zeolite, and such a release of nitrogen monoxide may have a different rate profile.

The zeolite framework may also be chosen to vary the rate of release of nitrogen monoxide. Zeolite frameworks are available in the form of synthetic materials having different structures (Atlas of Zeolite Framework types, fifth Revised Edition, Ch. Baerlocher, W.M. Meier, D.H. Olson, 2001, Elsevier). For example, the size of the pores and of the channels of the zeolite framework may be varied. For example, zeolite having the LTA structure has apertures defined by 8 pore tetrahedral units (i.e. a ring of 8 atoms of Si/Al and 8 oxygen atoms). MFI zeolite has a larger ring aperture defined by 10 tetrahedral units, and FAU by an even larger pore aperture of 12 tetrahedral units. The spatial configuration of the pores may also differ from one zeolite to another. For example, certain zeolites have channels that extend in only one direction (one-dimensional channel systems), whereas others have channel systems that interact in two or three dimensions (two-dimensional or three-dimensional channel systems). The size, form and spatial configuration of the zeolites may affect the rates of diffusion and of adsorption/desorption of the nitrogen monoxide (NO) and may be used to control the rate of release of NO.

Consequently, the composition of the zeolite material may be adapted so as to control the amount of nitrogen monoxide charged into the zeolite structure and/or the rate at which the nitrogen monoxide is released from the zeolite.

Such zeolite structures may be chosen, without being limited thereto, from the frameworks having the following three-letter codes: LTA, FAU, MFI, MOR, FER, BEA, PEI and SAS (see the website of the International Zeolite Association, www.iza-online.org, for further details regarding the correspondence of the codes with the framework structures of zeolites). These three-letter codes describe the framework architecture of zeolites, i.e. their structure, but do not describe the composition of the zeolite, which may vary greatly. The three-letter codes are used as a nomenclature system for zeolites.

The zeolites used in the present invention may have the general formula (I) below:

$$[(M_1^{n+})_{x/n}(M_2^{p+})_{y/p}\ldots(M_n^{q+})_{v/q}][Al_zSi_{1-z}O_4] \quad (I)$$

in which $M_1$ and $M_2$ to $M_n$ are independently chosen from

- metal cations external to the framework independently chosen from the group consisting of Li, Na, K, Mn, Ca, Mg, Fe, Cu, Ru, Rh, Co, Ni, Zn and Ag, and
- organic cations such as $N(R_1)_a(R_2)_b^+$ in which $R_1$ and $R_2$ are independently chosen from H, $-CH_3$, $-CH_2CH_3$ and $-CH_2CH_2CH_3$, and a and b are independently 0, 1, 2, 3 or 4 such that $a + b = 4$, for instance $NH_4^+$,

x ranges from 0 to nz, y ranges from 0 to pz, and v ranges from 0 to qz, on condition that $x/n + y/p +\ldots+ v/q = z$,

z is the number of silicon atoms replaced with aluminium atoms in the zeolite framework,

n+, p+ and q+ are, independently, integers +1, +2 or +3, when the associated cation is a metal cation, or equal to +1 when the associated cation is an organic cation.

The zeolites used in the present invention may have the general formula (II) below:

$$[(M_1^{n+})_{x/n}(M_2^{p+})_{y/p}][Al_zSi_{1-z}O_4] \quad \text{(II)}$$

in which $M_1$ and $M_2$ are as defined above,

x ranges from 0 to nz, and

y ranges from 0 to pz, on condition that $x/n + y/p = z$.

Preferably, the extraframework metal cations are cations of elements Zn or Mn, more preferably of Zn.

The zeolites may be prepared by ion exchange according to the method described in the book Verified Synthesis of Zeolitic Materials, by Robson H. and Lillerud, K.P., second revised edition, International Zeolite Association, 2001, www.iza-synthesis.org.

Reference may also be made to the examples in patent application WO 05/003032, the content of which is incorporated into the present patent application by reference.

Before charging with nitrogen monoxide, the zeolites may be fully or partially dehydrated, for example under vacuum, to remove the water from the zeolite channels. The resulting zeolite may then be exposed to nitrogen monoxide. Typically, the charging with nitrogen monoxide is performed at a temperature of from -100°C to 50°C. The charging with nitrogen monoxide may be performed with pure NO or with a mixture of NO and of a vector gas such as an inert gas, for example helium, argon or another inert gas, including mixtures thereof. The charging is typically performed at a pressure of between atmospheric pressure and a pressure of 10 bar.

The nitrogen monoxide starts to be released when the cosmetic composition is applied to the keratin materials.

The nitric oxide-charged zeolite may be prepared in powder form or in monolithic form. The monoliths may be formed by compressing a zeolite powder or by mixing a pulverulent zeolite with a suitable binder. The suitable binders include, without being limited thereto, ceramic binders, for example silica or alumina, and polymeric binders, for example polysulfone, polyethylene, PET, polystyrene, polytetrafluoroethylene (PTFE) and other polymers.

According to another embodiment, the microporous crystalline solid material is a zeotype.

The term "zeotypes" refers to crystalline structures of zeolites type in which all or some of the silicon and/or aluminium atoms are replaced with one or more atoms of elements from columns 2 to 13 of the Periodic Table, in particular with boron(III), gallium(III), iron(III), chromium(III, IV or V), germanium(IV), titanium(IV), vanadium(IV or V), cobalt(II) or cobalt(III) atoms. The zeotype may be silicalite (see the article by C. Lamberti, S. Bordiga and A. Zecchina published in the review Rassegna

Scientifica, vol. 4, No. 2, December 1999, the content of which is incorporated into the present patent application by reference).

Processes for preparing titanium and iron zeotypes are described, respectively, in patent applications US 4 480 135 and US 5 110 995. In particular, patent application US 4 480 135 describes the preparation of a titanium silicalite (TS-1) from a reaction mixture comprising a silicon oxide, a titanium oxide, optionally an alkali metal oxide, a nitrogenous organic base and water. Patent application US 5 110 995 describes the preparation of an iron zeotype starting with a mixture comprising a source of silica, a source of iron and, if necessary, a source of $El^{n+}$ (in which El is an element from periods 2, 3, 4 or 5 of the Periodic Table of the Elements), a base, an organic surfactant, and optionally a crystallization seed.

The zeolite containing absorbed nitrogen monoxide may be present in the composition in an amount sufficient to improve keratin tissues such as the skin, the hair, the lips, the nails, the eyelashes and the eyebrows.

In particular, the zeolite containing adsorbed nitrogen monoxide is in an amount sufficient to improve the appearance of the lips or the contour of the lips, especially to increase the volume of the lips and/or to model them and/or to make them smoother. The zeolite containing absorbed nitrogen monoxide may also be in an amount sufficient to modify the colour of the lips, to make them pinker or more vivid, or even to obtain a bitten lip effect.

In one embodiment, the zeolite containing adsorbed nitrogen monoxide is in an amount sufficient to delay, minimize, efface and/or prevent the signs of ageing of the skin, in particular the visible and/or palpable discontinuities of the texture of the skin associated with ageing, thus giving an improvement in the appearance and/or feel of the skin, for example a smoother, more uniform appearance and/or feel.

In one embodiment, the zeolite containing adsorbed nitrogen monoxide is in an amount sufficient to stabilize or remodel the hypodermic fat or deeper fat.

**Dyestuff**

The dyestuff may be any mineral and/or organic compound, having an absorption between 350 and 700 nm, or capable of generating an optical effect, for instance reflection of incident light or interference.

The dyestuffs that are useful in the present invention are chosen from any organic and/or mineral pigment known in the art, especially those described in Kirk-Othmer's Encyclopaedia of Chemical Technology and in Ullmann's Encyclopaedia of Industrial Chemistry.

For a composition in paste or cast form such as lipsticks or makeup products, from 0.5% to 50%, preferably from 2% to 40% and better still from 5% to

30% of dyestuff is generally used, relative to the total weight of the composition.

The dyestuffs may be mineral and/or organic.

Examples of mineral dyestuffs that may be mentioned include titanium dioxide, optionally surface-treated, zirconium oxide or cerium oxide, iron oxide or chromium oxide, manganese violet, ultramarine blue, chromium hydrate and ferric blue. For example, the following mineral pigments may be used: $Ta_2O_5$, $Ti_3O_5$, $Ti_2O_3$, TiO, $ZrO_2$ as a mixture with $TiO_2$, $ZrO_2$, $Nb_2O_5$, $CeO_2$, ZnS.

Examples of organic dyestuffs that may be mentioned include nitroso, nitro, azo, xanthene, quinoline, anthraquinone and phthalocyanin compounds, compounds of metallic complex type, and isoindolinone, isoindoline, quinacridone, perinone, perylene, diketopyrrolopyrrole, thioindigo, dioxazine, triphenylmethane and quinophthalone compounds.

In particular, the dyestuffs may be chosen from carmine, carbon black, aniline black, azo yellow, quinacridone, phthalocyanin blue, sorghum red, the blue pigments codified in the Color Index under the references CI 42090, 69800, 69825, 73000, 74100, 74160, the yellow pigments codified in the Color Index under the references CI 11680, 11710, 15985, 19140, 20040, 21100, 21108, 47000, 47005, the green pigments codified in the Color Index under the references CI 61565, 61570, 74260, the orange pigments codified in the Color

Index under the references CI 11725, 15510, 45370, 71105, the red pigments codified in the Color Index under the references CI 12085, 12120, 12370, 12420, 12490, 14700, 15525, 15580, 15620, 15630, 15800, 15850, 15865, 15880, 17200, 26100, 45380, 45410, 58000, 73360, 73915, 75470, the pigments obtained by oxidative polymerization of indole or phenolic derivatives as described in patent FR 2 679 771.

The pigments in accordance with the invention may also be in the form of composite pigments as described in patent EP 1 184 426. These composite pigments may be composed especially of particles comprising a mineral core, at least one binder for binding the organic pigments to the core, and at least one organic pigment at least partially covering the core.

The dyestuffs may be chosen from dyes, lakes and pigments.

The dyes are, for example, liposoluble dyes, although water-soluble dyes may be used. The liposoluble dyes are, for example, Sudan red, D&C Red 17, D&C Green 6, β-carotene, soybean oil, Sudan brown, D&C Yellow 11, D&C Violet 2, D&C Orange 5, quinoline yellow and annatto. They may represent from 0 to 20% and better still from 0.1% to 6% of the weight of the composition. The water-soluble dyes are especially beetroot juice or methylene blue, and may represent from 0.1% to 6% by weight of the composition (if present).

The term "lakes" means dyes adsorbed onto insoluble particles, the assembly thus obtained remaining insoluble during use. The mineral substrates onto which the dyes are adsorbed are, for example, alumina, silica, calcium sodium borosilicate or calcium aluminium borosilicate, and aluminium. Among the organic dyes that may be mentioned is cochineal carmine.

Examples of lakes that may be mentioned include the products known under the following names: D & C Red 21 (CI 45 380), D & C Orange 5 (CI 45 370), D & C Red 27 (CI 45 410), D & C Orange 10 (CI 45 425), D & C Red 3 (CI 45 430), D & C Red 7 (CI 15 850:1), D & C Red 4 (CI 15 510), D & C Red 33 (CI 17 200), D & C Yellow 5 (CI 19 140), D & C Yellow 6 (CI 15 985), D & C Green (CI 61 570), D & C Yellow 1 O (CI 77 002), D & C Green 3 (CI 42 053), D & C Blue 1 (CI 42 090).

The term "pigments" should be understood as meaning white or coloured, mineral or organic particles intended to colour and/or opacify the composition. The pigments in accordance with the invention may be chosen, for example, from white or coloured pigments, and pigments with special effects such as nacres, reflective pigments or interference pigments.

As pigments that may be used in the invention, mention may be made of titanium oxide, zirconium oxide or cerium oxide, and also zinc oxide, iron oxide or chromium oxide and ferric blue. Among the organic pigments that may be used in the invention, mention may be made of carbon black and barium, strontium, calcium (D&C Red No. 7) or aluminium lakes.

The nacres or nacreous pigments are iridescent particles, especially produced by certain molluscs in their shell or else synthesized.

The nacres may be present in the composition in a proportion of from 0.001% to 20% and preferably in a proportion of from 1% to 15% of the total weight of the composition. Among the nacres that may be used in the invention, mention may be made of mica coated with titanium oxide, with iron oxide, with natural pigment or with bismuth oxychloride, such as coloured titanium mica.

The pigments may be present in the composition in a proportion of from 0.05% to 30% and preferably in a proportion of from 2% to 20% of the weight of the final composition.

The variety of pigments that may be used in the present invention makes it possible to obtain a wide range of colours, and also particular optical effects such as metallic or interference effects.

The term "pigments with special effects" means pigments that generally create a coloured appearance (characterized by a certain shade, a certain vivacity and a certain level of luminance) that is non-uniform and that changes as a function of the conditions of observation (light, temperature, angles of observation, etc.). They are consequently in contrast with white or coloured pigments, which afford a standard opaque, semi-transparent or transparent uniform shade.

Examples of pigments with special effects that may be mentioned include white nacreous pigments such as mica coated with titanium or with bismuth oxychloride, coloured nacreous pigments such as mica coated with titanium and with iron oxides, mica coated with titanium and especially with ferric blue or with chromium oxide, mica coated with titanium and with an organic pigment as defined above, and also nacreous pigments based on bismuth oxychloride. Nacreous pigments that may be mentioned include the nacres Cellini sold by Engelhard (Mica-$TiO_2$-lake), Prestige sold by Eckart (Mica-$TiO_2$) and Colorona sold by Merck (Mica-$TiO_2$-$Fe_2O_3$).

Mention may also be made of pigments with an interference effect not bound to a substrate, for instance liquid crystals (Helicones HC from Wacker), holographic interference flakes (Geometric Pigments or Spectra f/x from Spectratek). The pigments with special effects also comprise fluorescent pigments, whether they are substances that are fluorescent in daylight or that produce ultraviolet fluorescence, phosphorescent pigments, photochromic pigments and thermochromic pigments.

The composition advantageously contains goniochromatic pigments, for example multilayer interference pigments and/or reflective pigments. These two types of pigment are described in patent application FR 0 209 246, the content of which is incorporated by reference into the present patent application.

The composition may contain reflective pigments, which may or may not be goniochromatic pigments, and may or may not be interference pigments.

Their size is compatible with the exhibition of a specular reflection of visible light (400-700 nm) of sufficient intensity, taking into account the mean gloss of the composition, to create a bright spot. This size can vary according to the chemical nature of the particles, their shape and their capacity for specular reflection of visible light.

The reflective particles will preferably have a size of at least 10 µm, for example between about 20 µm and about 50 µm.

The term "size" denotes the size given by the statistical particle size distribution to half of the population, which is noted D50. The size of the reflective particles may depend on their surface state. The more reflective this surface state, the smaller may be the size, in principle, and vice versa.

Reflective particles that may be used in the invention, with a metallic or white glint, may, for example, reflect the light in all the components of the visible range without significantly absorbing one or more wavelengths. The spectral reflectance of these reflective particles may, for example, be greater than 70%, and better still at least 80%, or even 90% or 95%, in the 400-700 nm range.

Whatever their shape, the reflective particles may or may not have a multilayer structure, and, in the case of a multilayer structure, for example at least one layer of uniform thickness, especially of a reflective material, which coats a substrate.

The substrate may be chosen from glasses, ceramics, graphite, metal oxides, aluminas, silicas, silicates, especially aluminosilicates and borosilicates and synthetic mica, this list not being limiting.

The reflective material may comprise a layer of metal or of a metallic compound.

The layer of metal or of metallic compound may or may not totally coat the substrate, and the layer of metal may be at least partially coated with a layer of another material, for example a transparent material. It may be preferable for the layer of metal or of metallic compound to totally coat the substrate, directly or indirectly, i.e. with insertion of at least one intermediate metallic or non-metallic layer.

The metal may be chosen, for example, from Ag, Au, Cu, Al, Ni, Sn, Mg, Cr, Mo, Ti, Pt, Va, Rb, W, Zn, Ge, Te, Se and alloys thereof. Ag, Au, Al, Zn, Ni, Mo, Cr, Cu and alloys thereof (for example bronzes and brasses) are preferred metals.

In the case especially of particles with a substrate coated with silver or gold, the metallic layer may be present in a content representing, for example, from 0.1% to 50% or even between 1% and 20% of the total weight of the particles.

Particles of glass coated with a metallic layer are described especially in documents JP-A-09 188 830, JP-A-10 158 450, JP-A-10 158 541, JP-A-07 258 460 and JP-A-05 017 710.

Particles with a glass substrate coated with silver, in the form of platelets, are sold under the name Microglass Metashine REFSX 2025 PS by the company Toyal. Particles with a glass substrate coated with nickel/chromium/molybdenum alloy are sold under the name Crystal Star GF 550 and GF 2525 by this same company.

Irrespective of their shape, the reflective particles may also be chosen from particles with a synthetic substrate coated at least partially with at least one layer of at least one metallic compound, especially a metal oxide, chosen, for example, from titanium oxides, especially $TiO_2$, iron oxides, especially $Fe_2O_3$, tin oxide, chromium oxide, barium sulfate and the following compounds: $MgF_2$, $CrF_3$, 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 or alloys thereof.

Examples of such particles that may be mentioned include particles comprising a synthetic mica substrate coated with titanium dioxide, or particles of glass coated either with brown iron oxide or with titanium oxide, tin oxide or a mixture thereof, for instance those sold under the brand name Reflecks® by the company Engelhard.

Pigments of the Metashine 1080R range sold by the company Nippon Sheet Glass Co. Ltd., are also suitable for the invention. These pigments, described more particularly in patent application JP 2001-11340, are flakes of C-Glass comprising 65% to 72% $SiO_2$, coated with a layer of titanium oxide of rutile type ($TiO_2$). These glass flakes have a mean thickness of 1 micron and a mean size of 80 microns, i.e. a mean size/mean thickness ratio of 80. They have blue, green, yellow or silvery glints depending on the thickness of the $TiO_2$ layer.

Mention may also be made of particles of between 80 and 100 µm in size, comprising a synthetic mica substrate (fluorophlogopite) coated with titanium dioxide representing 12% of the total weight of the particle, sold under the name Prominence by the company Nihon Koken.

The reflective particles may also be chosen from particles formed by a stack of at least two layers with different refractive indices. These layers may be of polymeric or metallic nature and may especially include at least one polymer layer. Such particles are described especially in WO 99/36477, US 6 299 979 and US 6 387 498. As illustrations of the materials that can constitute the various layers of the multilayer structure, it is possible to mention, this list not being limiting: polyethylene naphthalate (PEN) and its isomers, polyalkylene terephthalates and polyimides. Reflective particles comprising a stack of at least two layers of polymers are sold by the company 3M under the name Mirror Glitter. These particles comprise layers of 2,6-PEN and of polymethyl methacrylate in an 80/20 mass ratio. Such particles are described in patent US 5 825 643.

The composition may contain one or more goniochromatic pigments.

The goniochromatic colouring agent may be chosen, for example, from multilayer interference structures and liquid-crystal colouring agents.

In the case of a multilayer structure, it may comprise, for example, at least two layers, each layer, which may or may not be independent of the other layer(s), being made, for example, from at least one material chosen from the group consisting of the following materials: $MgF_2$, $CeF_3$, ZnS, ZnSe, Si, $SiO_2$, Ge, Te, $Fe_2O_3$, Pt, Va, $Al_2O_3$, MgO, $Y_2O_3$, $S_2O_3$, SiO, $HfO_2$, $ZrO_2$, $CeO_2$, $Nb_2O_5$, $Ta_2O_5$, $TiO_2$, Ag, Al, Au, Cu, Rb, Ti, Ta, W, Zn, $MoS_2$, cryolite, and alloys, polymers and combinations thereof.

The multilayer structure may or may not have, relative to a central layer, symmetry in the chemical nature of the stacked layers.

Examples of symmetrical multilayer interference structures that may be used in the compositions prepared in accordance with the invention are, for example, the following structures: $Al/SiO_2/Al/SiO_2/Al$, pigments having this structure being sold by the company Dupont de Nemours; $Cr/MgF_2/Al/MgF_2/Cr$, pigments having this structure being sold under the name Chromaflair by the company Flex; $MoS_2/SiO_2/Al/SiO_2/MoS_2$; $Fe_2O_3/SiO_2/Al/SiO_2/Fe_2O_3$, and $Fe_2O_3/SiO_2/Fe_2O_3/SiO_2/Fe_2O_3$, pigments having these structures being sold under the name Sicopearl by the company BASF; $MoS_2/SiO_2$/mica-oxide/$SiO_2/MoS_2$; $Fe_2O_3/SiO_2$/mica-oxide/$SiO_2/Fe_2O_3$; $TiO_2/SiO_2/TiO_2$ and $TiO_2/Al_2O_3/TiO_2$, $SnO/TiO_2/SiO_2/TiO_2/SnO$; $Fe_2O_3/SiO_2/Fe_2O_3$; SnO/mica/$TiO_2/SiO_2/TiO_2$/mica/SnO, pigments having these structures being sold under the name Xirona by the company Merck (Darmstadt). By way of example, these pigments may be pigments of silica/titanium oxide/tin oxide structure sold under the name Xirona Magic by the company Merck, pigments of silica/brown iron oxide structure sold under the name Xirona Indian Summer by the company Merck, and pigments of silica/titanium oxide/mica/tin oxide structure sold under the name

Xirona Caribbean Blue by the company Merck. Mention may also be made of the Infinite Colors pigments from the company Shiseido. Depending on the thickness and the nature of the various layers, different effects are obtained. Thus, with the $Fe_2O_3/SiO_2/Al/SiO_2/Fe_2O_3$ structure, the colour changes from green-golden to red-grey for $SiO_2$ layers of 320 to 350 nm; from red to golden for $SiO_2$ layers of 380 to 400 nm; from violet to green for $SiO_2$ layers of 410 to 420 nm; from copper to red for $SiO_2$ layers of 430 to 440 nm.

Goniochromatic colouring agents with a multilayer structure comprising an alternation of polymer layers, for example of the type such as polyethylene naphthalate and polyethylene terephthalate, may also be used. Such agents are described especially in WO-A-96/19347 and WO-A-99/36478.

Examples of pigments with a polymeric multilayer structure that may be mentioned include those sold by the company 3M under the name Color Glitter.

The liquid-crystal colouring agents comprise, for example, silicones or cellulose ethers onto which are grafted mesomorphic groups.

Examples of liquid-crystal goniochromatic particles that may be used include, for example, those sold by the company Chenix and also the products sold under the name Helicone® HC by the company Wacker.

The composition may also comprise dispersed goniochromatic fibres. Such fibres may, for example, have a size of between 200 µm and 700 µm, for example about 300 µm.

Interference fibres with a multilayer structure may be used in particular. Fibres with a multilayer structure of polymers are described especially in documents EP-A-921 217, EP-A-686 858 and US-A-5 472 798. The multilayer structure may comprise at least two layers, each layer, which may or may not be independent of the other layer(s), being made of at least one synthetic polymer. The polymers present in the fibres may have a refractive index ranging from 1.30 to 1.82 and better still ranging from 1.35 to 1.75. The polymers that are preferred for making the fibres are polyesters such as polyethylene terephthalate, polyethylene naphthalate, polycarbonate; acrylic polymers such as polymethyl methacrylate; polyamides.

Goniochromatic fibres with a polyethylene terephthalate/nylon-6 two-layer structure are sold by the company Teijin under the name Morphotex.

The composition may contain at least one fatty substance chosen from oils, waxes and pasty fatty substances.

**Oil**

According to one embodiment of the invention, the composition comprises at least one oil. This oil preferably represents at least 5% by weight and preferably at least 10% by weight relative to the total weight of the composition.

The composition may comprise a polar or apolar oil, or a mixture of the two. The term "polar oil" means an oil composed of chemical compounds comprising at least one polar group. The polar groups are well known to those skilled in the art; they may be, for example, groups of alcohol, ester or carboxylic acid type.

The apolar oils comprise oils that have a mean solubility parameter at 25°C of $\delta_a = 0\ (J/cm^3)^{½}$.

The sparingly polar oils comprise oils that have a mean solubility parameter at 25°C of: $0 < \delta_a < 5.0\ (J/cm^3)^{½}$, especially less than or equal to 4.9, better still less than or equal to 4.5 and better still less than or equal to 4.0 $(J/cm^3)^{½}$.

The highly polar oils have a mean solubility parameter $\delta_a$ according to the Hansen solubility space, at 25°C, of: $\delta_a \geq 5.0\ (J/cm^3)^{½}$, especially greater than or equal to 5.3, better still greater than or equal to 5.5 and better still greater than or equal to 6.0 $(J/cm^3)^{½}$, better still greater than or equal to 7.0 $(J/cm^3)^{½}$.

The definition and calculation of the solubility parameters in the three-dimensional Hansen solubility space are described in the article by C.M. Hansen: "The three dimensional solubility parameters"

J. Paint Technol. 39, 105 (1967).

According to this Hansen space:

- $\delta_D$ characterizes the London dispersion forces derived from the formation of dipoles induced during molecular impacts;
- $\delta_p$ characterizes the Debye interaction forces between permanent dipoles and the Keesom interaction forces between induced dipoles and permanent dipoles;
- $\delta_h$ characterizes the specific interaction forces (such as hydrogen bonding, acid/base, donor/acceptor, etc.);
- $\delta_a$ is determined by the equation: $\delta_a = (\delta_p^2 + \delta_h^2)^{½}$.

The parameters $\delta_p$, $\delta_h$, $\delta_D$ and $\delta_a$ are expressed in $(J/cm^3)^{½}$.

When the oily phase is a mixture of different oils, the solubility parameters of the mixture are determined from those of the compounds taken separately, according to the following relationships:

$$\delta_{Dmixt} = \sum_i xi\ \delta_{Di};\ \delta_{pmixt} = \sum_i xi\ \delta_{pi} \text{ and } \delta_{hmixt} = \sum_i xi\ \delta_{hi}$$

$$\delta_{amixt} = (\delta^2_{pmixt} + \delta^2_{hmixt})^{½}$$

in which xi represents the volume fraction of compound i in the mixture.

It is within the capability of a person skilled in the art to determine the amounts of each oil to obtain an oily phase that satisfies the desired criteria.

The apolar or sparingly polar oil may be a hydrocarbon-based oil.

The term "hydrocarbon-based oil" means an oil formed essentially from, or even consisting of, carbon and hydrogen atoms, and possibly oxygen or nitrogen atoms, and containing no silicon or fluorine atoms. It may contain alcohol, ester, ether, carboxylic acid, amine and/or amide groups.

The apolar or sparingly polar oil may be non-volatile.

The term "non-volatile oil" means any oil having a non-zero vapour pressure at room temperature and atmospheric pressure, of less than 0.02 mmHg and better still less than $10^{-3}$ mmHg.

The composition advantageously contains an apolar oil or a sparingly polar oil or a mixture of the two. The oil or the mixture of oil(s) advantageously represents at least 5% by weight relative to the total weight of the composition. The apolar oil and/or the sparingly polar oil advantageously represent(s) 5% to 99% by weight, for example from 10% to 85% by weight or even from 15% to 80% by weight relative to the total weight of the composition.

According to one embodiment, the oil is chosen from non-volatile hydrocarbon-based apolar oils, for example from linear or branched saturated alkanes. According to one embodiment, the oil is chosen from linear or branched hydrocarbons such as liquid paraffins, liquid petroleum jelly and liquid naphthalene, hydrogenated polyisobutene, isoeicosane, squalane and decene/butene copolymers, and mixtures thereof.

According to one embodiment, the fatty phase comprises from 30% to 70% by weight of apolar non-volatile hydrocarbon-based oil(s) relative to the weight of the fatty phase and preferably from 40% to 60% by weight relative to the weight of the fatty phase.

The composition advantageously contains an amount of non-volatile highly polar oil sufficient to disperse the crystalline solid material containing nitrogen monoxide.

These non-volatile highly polar oils may represent from 0.1% to 30% of the total weight of the composition, for example from 1% to 20% and especially about 10% by weight relative to the total weight of the composition.

The composition may thus contain an oily phase, comprising one or more oils, which may themselves be polar or apolar, and volatile or non-volatile.

These oils may be chosen, alone or as a mixture, from volatile and non-volatile oils of animal, plant, mineral or synthetic origin.

Mention may be made especially of:

- animal or plant oils, especially formed from fatty acid esters of polyols, in particular liquid triglycerides, for example sunflower oil, corn oil, soybean oil, marrow oil, grapeseed oil, sesame seed oil, hazelnut oil, apricot oil, almond oil or avocado oil; fish oils or glyceryl tricaprocaprylate, or oils of plant or animal origin of formula $R_1COOR_2$ in which $R_1$ represents a higher fatty acid residue containing from 7 to 19 carbon atoms and $R_2$ represents a branched hydrocarbon-based chain containing from 3 to 20 carbon atoms, for example Purcellin oil; liquid paraffin, liquid petroleum jelly, beauty-leaf oil, macadamia oil, rapeseed oil, coconut oil, groundnut oil, palm oil, castor oil, jojoba oil, olive oil or cereal germ oil; shea butter oil; perhydrosqualene;

- synthetic esters and ethers, especially of fatty acids, for instance the oils of formula $R_1COOR_2$ in which $R_1$ represents a higher fatty acid residue containing from 7 to 29 carbon atoms and $R_2$ represents a hydrocarbon-based chain containing from 3 to 30 carbon atoms, for instance isopropyl myristate, 2-ethylhexyl palmitate, 2-octyldodecyl stearate, 2-octyldodecyl erucate, isononyl isononanoate or isostearyl isostearate; hydroxylated esters, for instance isostearyl lactate, octyl hydroxystearate, octyldodecyl hydroxystearate, diisostearyl malate, triisocetyl citrate, and fatty alkyl heptanoates, octanoates and decanoates; polyol esters, for instance propylene glycol dioctanoate, neopentyl glycol diheptanoate or diethylene glycol diisononanoate; pentaerythritol esters, for instance pentaerythrityl tetraisostearate; esters of the type such as tridecyl trimellitate;

- fatty alcohols containing from 12 to 26 carbon atoms, for instance octyldodecanol, 2-butyloctanol, 2-hexyldecanol, 2-undecylpentadecanol or oleyl alcohol;
- linear or branched hydrocarbons of mineral or synthetic origin, such as liquid paraffins and derivatives thereof, liquid petroleum jelly, polydecenes, and hydrogenated polyisobutene such as parleam; isoparaffins, for instance isohexadecane and isodecane;
- glycerides and especially acetylglycerides or triglycerides of fatty acids containing 4 to 10 carbon atoms, for instance heptanoic, octanoic and capric/caprylic acid triglycerides.

Among the polar oils that are particularly preferred, mention may be made of octyldodecanol, hexyldecanol, octyldecanol, oleyl alcohol, castor oil, diisostearyl malate, glyceryl triheptanoate, glyceryl trioctanoate, capric/caprylic acid triglyceride, triisononanoin and tridecyl trimellitate, and mixtures thereof.

Among the apolar oils that are particularly preferred, mention may be made of aliphatic hydrocarbons, especially of $C_6$-$C_{40}$, for instance volatile liquid paraffins, such as isohexadecane or isododecane, or non-volatile liquid paraffins, and derivatives thereof; liquid petroleum jelly, hydrogenated or non-hydrogenated polydecenes, hydrogenated polyisobutene such as parleam oil, squalane, polybutylenes and isononyl isononanoate; fluoro oils and especially perfluoro oils, and mixtures thereof.

Mention may be made especially of the following oils:

| | $\delta_a$ $(J/cm^3)^{1/2}$ |
|---|---|
| Castor oil | 9.09 |
| 2-Hexyldecanol | 8.55 |
| Oleyl alcohol | 8.17 |
| Octyldodecanol | 7.69 |
| Heptanoic acid triglyceride | 7.29 |
| Diisostearyl malate | 7.19 |
| Octanoic acid triglyceride | 6.87 |
| Capric/caprylic acid triglyceride | 6.69 |
| Triisononanoin | 6.54 |
| Tridecyl trimellitate | 5.35 |
| Isononyl isononanoate | 4.87 |
| Hydrogenated polyisobutene | 0 |
| Isododecane | 0 |

In addition, the composition may contain non-volatile silicone oils, for instance polyalkylmethyl-siloxanes substituted with functional groups such as hydroxyl, thiol and/or amine groups; or polysiloxanes modified with fatty acids, fatty alcohols or polyoxyalkylenes.

*Volatile oil of the fatty phase*

One or more volatile oils may be included in the fatty phase of the composition according to the invention. These oils may be hydrocarbon-based oils or silicone oils optionally comprising alkyl or alkoxy groups that are pendent or at the end of a silicone chain.

The term "volatile oil" means any oil having a vapour pressure, at room temperature and atmospheric pressure, of greater than 0.02 mmHg.

As volatile silicone oils that may be used in the invention, mention may be made of linear or cyclic silicones having a viscosity at room temperature of less than 8 cSt and especially containing from 2 to 7 silicon atoms, these silicones optionally comprising alkyl or alkoxy groups containing from 1 to 10 carbon atoms. As volatile silicone oils that may be used in the invention, mention may be made especially of octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, dodecamethylcyclohexasiloxane, heptamethylhexyltrisiloxane, heptamethyloctyltrisiloxane, octamethyltrisiloxane and decamethyltetrasiloxane, and mixtures thereof.

As volatile oils that may be used in the invention, $C_8$-$C_{16}$ isoalkane oils (also known as isoparaffins), for instance isododecane, isodecane and isohexadecane and, for example, the oils sold under the trade names Isopar and Permethyl, and especially isododecane (Permethyl 99 A), are especially preferred.

Preferably, the fatty phase of the composition contains less than 10% of one or more volatile oils. Preferably, the fatty phase contains less than 5%, less than 3% or even less than 1% of one or more volatile oils.

The composition of the invention may be in solid, pasty or more or less fluid liquid form. It may be a solid or soft anhydrous gel, a liquid oily phase or a mousse. It may be in the form of a solid composition and more especially in the form of a stick.

This phase is capable of forming a continuous phase and contains, as its name indicates, at least one non-aqueous organic solvent that is preferably a water-insoluble compound that is liquid at room temperature and atmospheric pressure.

The composition according to the invention may also comprise one or more cosmetically acceptable (acceptable tolerance, toxicology and feel) organic solvents.

These solvents may be generally present in a content ranging from 0.1% to 90%, more preferably from 10% to 90% and better still from 30% to 90% by weight relative to the total weight of the composition.

As solvents that may be used in the

composition of the invention, mention may be made, besides the hydrophilic organic solvents mentioned above, of ketones that are liquid at room temperature, such as methyl ethyl ketone, methyl isobutyl ketone, diisobutyl ketone, isophorone, cyclohexanone and acetone; propylene glycol ethers that are liquid at room temperature, such as propylene glycol monomethyl ether, propylene glycol monomethyl ether acetate and dipropylene glycol mono-n-butyl ether; short-chain esters (containing from 3 to 8 carbon atoms in total), such as ethyl acetate, methyl acetate, propyl acetate, n-butyl acetate and isopentyl acetate; ethers that are liquid at room temperature, such as diethyl ether, dimethyl ether and dichlorodiethyl ether; alkanes that are liquid at room temperature, such as decane, heptane, dodecane, isododecane and cyclohexane; cyclic aromatic compounds that are liquid at room temperature, such as toluene and xylene; aldehydes that are liquid at room temperature, such as benzaldehyde and acetaldehyde, and mixtures thereof.

The composition according to the invention is advantageously in anhydrous thickened form. Thus, the invention relates more especially to a thickened anhydrous lip makeup or lipcare composition containing at least one thickener chosen from fatty-phase-gelling agents, waxes and fillers, and mixtures thereof.

Oil-gelling agents that may be mentioned include optionally modified clays, for instance hectorites modified with a $C_{10}$ to $C_{22}$ fatty acid ammonium chloride, for instance hectorite modified with distearyldimethylammonium chloride; silica; partially or totally crosslinked elastomeric organopolysiloxanes of three-dimensional structure, for instance those sold under the names KSG6®, KSG16® and KSG18® from Shin-Etsu, Trefil E-505C® or Trefil E-506C® from Dow Corning, Gransil SR-CYC®, SR DMF 10®, SR-DC556®, SR 5CYC gel®, SR DMF 10 gel® and SR DC 556 gel® from Grant Industries and SF 1204® and JK 113® from General Electric; galactomannans comprising from one to six and in particular from two to four hydroxyl groups per saccharide, substituted with a saturated or unsaturated alkyl chain, for instance guar gum alkylated with $C_1$ to $C_6$ and in particular $C_1$ to $C_3$ alkyl chains, and more particularly ethyl guar with a degree of substitution of 2 to 3, such as the product sold by the company Aqualon under the name N-Hance-AG; gums and especially silicone gums, for instance PDMSs with a viscosity > 500 000 centistokes. These gelling agents are used, for example, in concentrations of from 0.2% to 15% of the total weight of the composition.

The composition according to the invention may also comprise at least one fatty substance that is solid at room temperature, especially chosen from waxes and pasty fatty substances, and mixtures thereof. These waxes may be of animal, plant, mineral or synthetic origin.

The composition may also contain at least one pasty compound.

For the purposes of the present invention, the term "pasty substance" is intended to denote a lipophilic fatty compound, with a reversible solid/liquid change of state, comprising at a temperature of 23°C a liquid fraction and a solid fraction. The term "pasty substance" also means polyvinyl laurate.

The pasty compound may be chosen from:

- lanolin and its derivatives,
- polymeric or non-polymeric fluoro compounds,
- polymeric or non-polymeric silicone compounds,
- vinyl polymers, especially:
    - olefin homopolymers
    - olefin copolymers
    - hydrogenated diene homopolymers and copolymers
    - homopolymeric or copolymeric linear or branched oligomers of alkyl (meth)acrylates preferably containing a $C_8$-$C_{30}$ alkyl group
    - homopolymeric and copolymeric oligomers of vinyl esters containing $C_8$-$C_{30}$ alkyl groups
    - homopolymeric and copolymeric oligomers of vinyl ethers containing $C_8$-$C_{30}$ alkyl groups
    - liposoluble polyethers resulting from polyetherification between one or more $C_2$-$C_{100}$ and preferably $C_2$-$C_{50}$ diols
    - esters

and mixtures thereof.

As illustrations of conventionally used lanolin derivatives, mention may be made especially of liquid lanolin, reduced lanolin, lanolin purified by adsorption, acetylated lanolin, oxypropylenated (5 OP) lanolin wax, liquid lanolin acetate, hydroxylanolin, polyoxyethylene-lanolin, lanolin fatty acid, hard lanolin fatty acid, cholesteryl esters of lanolin fatty acid, lanolin alcohol, lanolin alcohol acetate and isopropyl lanolate, and the like.

Among the liposoluble polyethers that are preferred in particular are copolymers of ethylene oxide and/or of propylene oxide with $C_6$-$C_{30}$ long-chain alkylene oxides, more preferably such that the weight ratio of the ethylene oxide and/or of the propylene oxide to the alkylene oxides in the copolymer is from 5:95 to 70:30. In this family, mention will be made especially of copolymers such that the long-chain alkylene oxides are arranged in blocks with a mean molecular weight of from 1000 to 10 000, for example a polyoxyethylene/polydodecyl glycol block copolymer such as the ethers of dodecanediol (22 mol) and of polyethylene glycol (45 EO) sold under the brand name Elfacos ST9 by Akzo Nobel.

Among the pasty esters that are especially preferred are:

- esters of an oligomeric glycerol, especially diglycerol esters, in particular condensates of adipic acid and of glycerol, for which some of the hydroxyl groups of the glycerols have reacted with a mixture of fatty acids such as stearic acid, capric acid, stearic acid and isostearic acid, and 12-hydroxystearic acid, especially like those sold under the brand name Softisan 649 by the company Sasol,

- the arachidyl propionate sold under the brand name Waxenol 801 by Alzo,
- phytosterol esters,
- non-crosslinked polyesters resulting from the polycondensation between a linear or branched $C_4$-$C_{50}$ dicarboxylic or polycarboxylic acid and a $C_2$-$C_{50}$ diol or polyol, other than the polyester described above,
- aliphatic esters of an ester resulting from the esterification of an ester of an aliphatic hydroxycarboxylic acid with an aliphatic monocarboxylic acid; and mixtures thereof, for instance
  - the ester resulting from the esterification reaction of hydrogenated castor oil with isostearic acid in proportions of 1 to 1 (1/1) or hydrogenated castor oil monoisostearate,
  - the ester resulting from the esterification reaction of hydrogenated castor oil with isostearic acid in proportions of 1 to 2 (1/2) or hydrogenated castor oil diisostearate,
  - the ester resulting from the esterification reaction of hydrogenated castor oil with

isostearic acid in proportions of 1 to 3 (1/3) or hydrogenated castor oil triisostearate,

- and mixtures thereof.

Among the pasty compounds of plant origin that will preferably be chosen is a mixture of soybean sterols and of oxyethylenated (5 EO) oxypropylenated (5 PO) pentaerythritol, sold under the reference Lanolide by the company Vevy.

The pasty compound preferably represents from 1% to 99%, better still from 1% to 60%, better still 2% to 30% and better still 5% to 15% by weight of the composition.

The composition according to the invention may also comprise one or more fillers, especially in a content ranging from 0.01% to 50% by weight and preferably ranging from 0.01% to 30% by weight relative to the total weight of the composition. The term "fillers" should be understood as meaning white or colourless, mineral or synthetic particles of any form, which are insoluble in the medium of the composition irrespective of the temperature at which the composition is manufactured. These fillers serve especially to modify the rheology or the texture of the composition.

The fillers may be mineral or organic of any form, platelet-shaped, spherical or oblong, irrespective of the crystallographic form (for example lamellar, cubic, hexagonal, orthorhombic, etc.). Mention may be made of talc, mica, silica, kaolin, polyamide (Nylon®) powder (Orgasol® from Atochem), poly-β-alanine powder and polyethylene powder, powders of tetrafluoroethylene polymers (Teflon®), lauroyllysine, starch, boron nitride, hollow polymer microspheres such as those of polyvinylidene chloride/acrylonitrile, for instance Expancel® (Nobel Industrie) or of acrylic acid copolymers (Polytrap® from the company Dow Corning) and silicone resin microbeads (for example Tospearls® from Toshiba), elastomeric polyorganosiloxane particles, precipitated calcium carbonate, magnesium carbonate, magnesium hydrogen carbonate, hydroxyapatite, hollow silica microspheres (Silica Beads® from Maprecos), glass or ceramic microcapsules, and metal soaps derived from organic carboxylic acids containing from 8 to 22 carbon atoms and preferably from 12 to 18 carbon atoms, for example zinc stearate, magnesium stearate or lithium stearate, zinc laurate or magnesium myristate, and Polypore® L200 (Chemdal Corporation). Mention may also be made of silica-based fillers, for instance Aerosil 200, Aerosil 300; Sunsphere L-31 and Sunsphere H-31 sold by Asahi Glass; Chemicelen sold by Asahi Chemical; composites of silica and of titanium dioxide, for instance the TSG series sold by Nippon Sheet Glass. Finally, mention may be made of polyurethane powders, in particular powders of crosslinked polyurethane comprising a copolymer, the said copolymer comprising trimethylol hexyllactone. In particular, it may be a polymer of hexamethylene diisocyanate/trimethylol hexyllactone. Such particles are especially commercially available, for example, under the name Plastic Powder D-400® or Plastic Powder D-800® from the company Toshiki.

The filler may be, for example a filler with a mean particle size of less than 100 µm and especially between 1 and 50 µm, for example between 4 and 20 µm.

**Tacky wax**

According to one embodiment, the composition comprises at least one "tacky" wax, i.e. a wax with a tack of greater than or equal to 0.1 N.s.

The wax is generally a lipophilic compound that is solid at room temperature (25°C), with a solid/liquid reversible change of state, having a melting point of greater than or equal to 30°C, which may be up to 120°C.

By bringing the wax to the liquid form (melting), it is possible to make it miscible with oils and to form a microscopically uniform mixture, but on cooling the mixture to room temperature, recrystallization of the wax in the oils of the mixture is obtained.

In particular, the waxes that are suitable for the invention may have a melting point of greater than 45°C approximately, better still greater than or equal to 50°C and in particular greater than or equal to 55°C.

The melting point of the wax may be measured using a differential scanning calorimeter (DSC), for example the calorimeter sold under the name MDSC 2929 by the company TA Instruments.

The measuring protocol is as follows:

A sample of 5 mg of product placed in a crucible is subjected to a first temperature rise ranging from 0°C to 120°C, at a heating rate of 10°C/minute, it is then cooled from 120°C to 0°C at a cooling rate of 10°C/minute and is finally subjected to a second temperature increase ranging from 0°C to 120°C at a heating rate of 5°C/minute. During the second temperature increase, the variation of the difference in power absorbed by the empty crucible and by the crucible containing the sample of product is measured as a function of the temperature. The melting point of the compound is the temperature value corresponding to the top of the peak of the curve representing the variation in the difference in absorbed power as a function of the temperature.

The waxes that may be used in the compositions according to the invention are chosen from waxes that are solid and rigid at room temperature, of animal, plant, mineral or synthetic origin, and mixtures thereof.

The tacky wax used may especially have a tack ranging from 0.1 N.s to 10 N.s, in particular ranging from 0.1 N.s to 5 N.s, preferably ranging from 0.2 N.s to 5 N.s and better still ranging from 0.3 N.s to 2 N.s.

The tack of the wax is determined by measuring the change in force (compression force or stretching force) as a function of time, at 20°C, using the texturometer sold under the name "TA-XT2®" by the company Rheo, equipped with a stainless-steel cylinder 2 mm in diameter.

The measuring protocol is as follows:

The wax is melted at a temperature equal to the melting point of the wax + 10°C. The molten wax is poured into a container 25 mm in diameter and 20 mm deep. The wax is recrystallized at room temperature (25°C) for 24 hours such that the surface of the wax is flat and smooth, and the wax is then stored for at least 1 hour at 20°C before measuring the tack.

The texturometer spindle is displaced at a speed of 0.1 mm/s then penetrates the wax to a penetration depth of 0.3 mm. When the spindle has penetrated the wax to a depth of 0.3 mm, the spindle is held still for 1 second (corresponding to the relaxation time) and is then withdrawn at a speed of 0.5 mm/s.

The tacky wax that may be used generally has a hardness of less than or equal to 3.5 MPa, in particular ranging from 0.01 MPa to 3.5 MPa, especially ranging from 0.05 MPa to 3 MPa.

The hardness is measured according to the protocol described above.

Tacky waxes that may be used include a $C_{20}$-$C_{40}$

alkyl (hydroxystearyloxy)stearate (the alkyl group containing from 20 to 40 carbon atoms), alone or as a mixture.

Such a wax is especially sold under the names "Kester Wax K 82 P®", and "Kester Wax K 80 P®" by the company Koster Keunen.

The waxes mentioned above generally have a starting melting point of less than 45°C.

The composition according to the invention may comprise a total content of waxes ranging from 5% to 50%, preferably from 5% to 40% by weight and more particularly from 10% to 35% by weight, relative to the total weight of the composition.

The wax(es) (including the tacky wax) may be present in the form of an aqueous microdispersion of wax. The expression "aqueous microdispersion of wax" means an aqueous dispersion of wax particles in which the size of the said wax particles is less than or equal to about 1 µm.

Wax microdispersions are stable dispersions of colloidal wax particles, and are described especially in "Microemulsions Theory and Practice", L.M. Prince Ed., Academic Press (1977) pages 21-32.

In particular, these wax microdispersions may be obtained by melting the wax in the presence of a surfactant, and optionally of a portion of water, followed by gradual addition of hot water with stirring. The intermediate formation of an emulsion of the water-in-oil type is observed, followed by a phase inversion, with final production of a microemulsion of the oil-in-water type. On cooling, a stable microdispersion of solid wax colloidal particles is obtained.

The wax microdispersions may also be obtained by stirring the mixture of wax, surfactant and water using stirring means such as ultrasound, high-pressure homogenizers or turbomixers.

The particles of the wax microdispersion preferably have mean sizes of less than 1 µm (especially ranging from 0.02 µm to 0.99 µm) and preferably less than 0.5 µm (especially ranging from 0.06 µm to 0.5 µm).

These particles consist essentially of a wax or a mixture of waxes. However, they may comprise a small proportion of oily and/or pasty fatty additives, a surfactant and/or a common liposoluble additive/active agent.

When the wax or the mixture of waxes is present in the compositions according to the invention in the form of an aqueous dispersion of particles, the size of the particles, expressed as the mean "effective" volume diameter D[4,3], may be advantageously less than or equal to 1 µm and especially less than or equal to 0.75 µm.

The wax particles may have varied shapes. They may especially be spherical.

The composition may contain at least one wax other than that mentioned above.

The wax may have a hardness ranging from 0.05 MPa to 30 MPa, the hardness being determined via the method described above for the fatty phase.

It is especially possible to use hydrocarbon-based waxes, for instance beeswax, lanolin wax, lemon wax, orange wax and Chinese insect waxes; rice bran wax, carnauba wax, candelilla wax, ouricury wax, Japan wax, berry wax, shellac wax and sumach wax; montan wax, microcrystalline waxes, paraffins and ozokerite; polyethylene wax, polymethylene wax, the waxes obtained by Fischer-Tropsch synthesis and waxy copolymers, and also esters thereof.

Mention may also be made of waxes obtained by catalytic hydrogenation of animal or plant oils containing linear or branched $C_8$-$C_{32}$ fatty chains.

Among these waxes that may especially be mentioned are hydrogenated jojoba oil, isomerized jojoba oil such as the trans-isomerized partially hydrogenated jojoba oil manufactured or sold by the company Desert Whale under the commercial reference Iso-Jojoba-50®, hydrogenated sunflower oil, hydrogenated castor oil, hydrogenated coconut oil, hydrogenated lanolin oil and bis(1,1,1-trimethylol-propane) tetrastearate sold under the name "Hest 2T-4S" by the company Heterene and bis(1,1,1-trimethylol-propane) tetrabehenate sold under the name Hest 2T-4B by the company Heterene.

Mention may also be made of silicone waxes and modified silicone waxes, for instance silicone-treated candelilla wax, and fluoro waxes.

The wax obtained by hydrogenation of olive oil esterified with stearyl alcohol, sold under the name "Phytowax Olive 18 L57" or else the waxes obtained by hydrogenation of castor oil esterified with cetyl alcohol sold under the names "Phytowax ricin 16L64 and 22L73" by the company Sophim may also be used. Such waxes are described in patent application FR-A-2 792 190.

According to one embodiment, the wax has a hardness of less than 4 MPa and preferably less than or equal to 3.5 MPa.

Such waxes are, for example, oxypropylenated lanolin wax (5 EO), orange wax, lemon wax, hydrogenated castor oil wax, the mixture of esters of aliphatic acids and of primary alcohols sold under the reference Burco LB-02, the olive wax (unsaponifiable matter of hydrogenated olive oil) sold under the reference Inholive by the company Exa International, the PDMS-grafted behenyl methacrylate wax sold under the reference KP-562 by the company Shin-Etsu, fluoropolymethylalkyldimethylsiloxane wax such as the product sold under the reference Wax 23087 by the company Wacker, C30-C45 alkyl dimethicone wax such as the product sold under the reference SF 1642 by GE Bayer, and ethoxylated bis(trimethylolpropane) tetrastearate (5 EO) such as the product sold under the reference SF 1642 by the company GE Bayer.

The composition may contain a micronized wax, also known as a microwax.

As microwaxes that may be used in the compositions according to the invention, mention may be made of carnauba microwaxes, such as the product sold under the name "MicroCare 350®" by the company Micro Powders, synthetic microwaxes, such as that product sold under the name "MicroEase 114S®" by the company Micro Powders, microwaxes consisting of a mixture of carnauba wax and polyethylene wax, such as the products sold under the names "Micro Care 300®" and "310®" by the company Micro Powders, microwaxes consisting of a mixture of carnauba wax and of synthetic wax, such as the product sold under the name "Micro Care 325®" by the company Micro Powders, polyethylene microwaxes, such as the products sold under the names "Micropoly 200®", "220®", "220L®" and "250S®" by the company Micro Powders, and polytetrafluoroethylene microwaxes such as the products sold under the names "Microslip 519®" and "519 L®" by the company Micro Powders.

Among the microwaxes mentioned above, some of them, for instance carnauba microwax, the synthetic microwax "MicroEase 114S®" or the microwax consisting of a mixture of carnauba wax and of synthetic wax "MicroCare 325®", have a starting melting point of greater than or equal to 45°C.

The composition according to the invention advantageously contains polyethylene wax with a weight-average molecular mass of between 300 and 700 and especially equal to 500 g/mol.

As a guide, the wax may represent from 0.01% to 65%, preferably from 2% to 50% and better still from 5% to 35% of the total weight of the composition.

The composition according to the invention may also contain ingredients commonly used in cosmetics, such as antioxidants.

## Fibres

The composition may contain fibres.

The term "fibre" should be understood as meaning an object of length L and diameter D such that L is very much greater than D, D being the diameter of the circle in which the cross section of the fibre is inscribed. In particular, the ratio L/D (or shape factor) is chosen within the range from 3.5 to 2500, preferably from 5 to 500 and better still from 5 to 150.

The fibres that may be used in the composition of the invention may be fibres of synthetic or natural, mineral or organic origin. In particular, the fibres have a length ranging from 1 µm to 10 mm, preferably from 0.1 mm to 5 mm and better still from 1 mm to 3.5 mm. Their cross section may be within a circle of diameter ranging from 2 nm to 500 μm, preferably ranging from 100 nm to 100 μm and better still from 1 μm to 50 μm. The weight or yarn count of the fibres is often given in denier or decitex and represents the weight in grams per 9 km of yarn. Preferably, the fibres according to the invention have a yarn count chosen within the range from 0.15 to 30 denier and better still from 0.18 to 18 denier.

The fibres may be those described in patent application EP 1 201 221, the content of which is incorporated into the present patent application by way of reference.

Preferably, fibres of synthetic origin and in particular organic fibres are used, for instance those used in surgery. Water-insoluble fibres may advantageously be used. The fibres that may be used in the composition according to the invention are preferably polyamide, cellulose, poly-p-phenyleneterephthamide or polyethylene fibres. Their length (L) may range from 0.1 mm to 5 mm and preferably from 0.25 mm to 1.6 mm, and their mean diameter may range from 1 μm to 50 μm. In particular, the polyamide fibres sold by Etablissements P. Bonte under the name "Polyamide 0.9 Dtex 3 mm", with a mean diameter of 6 μm, a yarn count of about 0.9 dtex and a length ranging from 0.3 mm to 5 mm, may be used. It is also possible to use poly-p-phenyleneterephthamide fibres with a mean diameter of 12 μm and a length of about

1.5 mm, for instance those sold under the name "Kevlar Floc" by the company DuPont Fibres, or else cellulose (or rayon) fibres with a mean diameter of 50 µm and a length ranging from 0.5 mm to 6 mm, for instance those sold under the name "Natural rayon flock fiber RC1BE - N003 - M04" by the company Claremont Flock. Polyethylene fibres may also be used, for instance those sold under the name "Shurt Stuff 13 099 F" by the company Mini Fibers.

The fibres may be present in the composition according to the invention in a content ranging from 0.01% to 10% by weight, preferably from 0.1% to 5% by weight and better still from 0.3% to 2% by weight relative to the total weight of the composition.

**Gelling agent**

The first composition may contain at least one gelling agent, which may be mineral or organic, and polymeric or non-polymeric. The gelling agent may be chosen to gel an aqueous phase or a fatty phase of the composition, depending on the case.

The term "gelling agent" means a compound that modifies the rheology of the medium into which it is incorporated.

The aqueous-medium gelling agent may be chosen from:

- hydrophilic clays,
- hydrophilic fumed silica,
- water-soluble cellulose-based thickeners,

- guar gum, xanthan gum, carob gum, scleroglucan gum, gellan gum, rhamsan gum, karaya gum or carrageenan gum,
- alginates, maltodextrins, starch and its derivatives, and hyaluronic acid and its salts,
- the polyglyceryl (meth)acrylate polymers sold under the names "Hispagel" or "Lubragel" by the companies Hispano Qimica or Guardian,
- polyvinylpyrrolidone,
- polyvinyl alcohol,
- crosslinked acrylamide polymers and copolymers, such as those sold under the names "PAS 5161" or "Bozepol C" by the company Hoechst, "Sepigel 305" by the company SEPPIC, or alternatively
- the crosslinked methacryloyloxyethyltrimethylammonium chloride homopolymers sold under the name "Salcare SC95" by the company Allied Colloid,
- associative polymers and especially associative polyurethanes.

Such gelling agents are described especially in patent application EP-A-1 400 234, the content of which is incorporated by way of reference.

The oily-medium gelling agent may be chosen from:

- organophilic clays;
- hydrophobic fumed silicas;
- alkyl guar gums (with a $C_1$-$C_6$ alkyl group), such as those described in EP-A-708 114;

- oil-gelling polymers, for instance triblock polymers or star polymers resulting from the polymerization or copolymerization of at least one monomer containing an ethylenic group, for instance the polymers sold under the name Kraton;
- polymers with a weight-average molecular mass of less than 100 000, comprising a) a polymer skeleton containing hydrocarbon-based repeating units containing at least one hetero atom, and optionally b) at least one pendent fatty chain and/or at least one terminal fatty chain, which are optionally functionalized, containing from 6 to 120 carbon atoms and being linked to these hydrocarbon-based units, as described in patent applications WO-A-02/056847 and WO-A-02/47619, the content of which is incorporated by way of reference; in particular, polyamide resins (especially comprising alkyl groups containing from 12 to 22 carbon atoms) such as those described in US-A-5 783 657, the content of which is incorporated by way of reference;
- the silicone-based polyamide resins as described in patent application EP-A-1 266 647 and in the French patent application filed under the number 0 216 039, the content of which is incorporated by way of reference.

Such gelling agents are especially described in patent application EP-A-1 400 234, the content of which is incorporated by way of reference.

The gelling agent may be an organic gelling agent, i.e. an agent comprising at least one organic compound.

The organogelling agents may be chosen from those described in patent application WO-A-03/105 788, the content of which is incorporated by way of reference.

Needless to say, a person skilled in the art will take care to select this or these optional additional compound(s), and/or the amount thereof, such that the advantageous properties of the corresponding composition according to the invention are not, or are not substantially, adversely affected by the envisaged addition.

The composition may be in any galenical form normally used for topical application, and especially in the form of an oily or aqueous solution, an oily or aqueous gel, or oil-in-water or water-in-oil emulsion, a multiple emulsion, a dispersion of oil in water by means of vesicles, the vesicles being at the oil/water interface, or a powder. Each first composition may be fluid or solid.

The first composition according to the invention may especially be in the form of a suspension, a dispersion, a solution, a gel, an emulsion, especially an oil-in-water (O/W) or water-in-oil (W/O) emulsion, or a multiple emulsion (W/O/W or polyol/O/W or O/W/O), in the form of a cream, a foam, a stick, a dispersion of vesicles, especially of ionic or nonionic lipids, a two-phase or multi-phase lotion, a spray, a powder, a paste, especially a soft paste (especially a paste having a dynamic viscosity at 25°C of about from 0.1 to 40 Pa.s at a shear rate of 200 $s^{-1}$, after 10 minutes of measurement in cone/plate geometry). The first composition may be a leave-in composition.

The first composition may have a continuous fatty phase; it may be in anhydrous form and may contain less than 5% water and better still less than 1% water relative to the total weight of the first composition, and may especially be water-free, the water not being added during the preparation of the first composition, but corresponding to the residual water provided by the mixed ingredients.

The first composition may have the appearance of a lotion, a cream, a pomade, a soft paste, an ointment, a solid cast or moulded especially as a stick or a dish, or a compacted solid.

The first composition is in the form of a more or less rigid stick.

The composition of the invention may be in the form of a coloured lip makeup product, for instance a lipstick or a lip gloss, having care or treatment properties.

The compositions of the present invention may be skincare preparations, for example exfoliant or scrubbing preparations, or exfoliant masks; facial makeup preparations in the form of creams, sticks or makeup powders; eye care preparations, for example eyeshadows, mascaras, eyeliners or eye creams; lipcare preparations, for example lipsticks, lip glosses or lip contour pencils; nailcare preparations such as colourless or coloured nail varnishes; foot care preparations, for example foot creams or foot balms, specific deodorants and antiperspirants or anti-callous preparations; photoprotective preparations such as antisun milks, lotions, creams and oils, sunscreens or "tropical" sun compositions, tan-generating compositions or after-sun preparations; tanning preparations, for example self-tanning creams; hair treatment or haircare preparations.

The composition according to the invention may be manufactured by means of the known processes generally used in cosmetics or dermatology. In particular, it may be obtained by heating the various constituents to the melting point of the highest-melting waxes, followed by casting the molten mixture in a mould (compact case or finger stall). It may also be obtained by extrusion as described in patent application EP-A-667 146.

The invention is illustrated in greater detail in the examples that follow. The percentages are given on a weight basis.

## Example 1: Preparation of Zn-NO and Mn-NO zeolites

The Zn-NO and Mn-NO zeolites are prepared according to Example 2b of patent application WO 2005/003032, which is incorporated herein by reference.

A zeolite-A synthesized according to the procedure given by Robson H. & Lillerud, K.P. in Verified syntheses of Zeolitic Materials, International Zeolite Association (2001); www .iza-synthesis.org, is used.

The sodium ions are then replaced with transition metal cations known for binding nitrogen monoxide (e.g.: $Mn^{2+}$ or $Zn^{2+}$), in order to obtain ion-exchange zeolites, according to the following protocol: sodium zeolite-A (5 g) is placed in a 0.05 M solution of metal acetate (400 ml, distilled water) and dried at 100°C overnight.

Analysis of the zeolites is performed using an Agilent 7500 ICP-MS spectrometer.

The zeolites A containing Mn or Zn, respectively, are then dehydrated.

0.3 g of Mn or Zn zeolite-A thus prepared is dehydrated for 2 hours at 300°C (0.5 mmHg). It is then cooled to room temperature and exposed to a nitrogen monoxide/helium gaseous mixture (10% NO, 90% He) at a pressure of 3 atmospheres for 10 minutes, and then exposed again to nitrogen monoxide at a pressure of 3 atmospheres. This step is repeated three times.

The capacity of the NO to be released in the presence of a flow of argon (either saturated with water vapour or taken directly from a gas cylinder, 5 ml min$^{-1}$) is then measured. The gas is then bubbled through a phosphate-buffered saline solution (pH 7.4, 10 ml) into which a precalibrated nitrogen monoxide electrode (World Precision Instruments, ISO-NO Mark II) is immersed. The concentration of NO released over time is thus measured.

**Example 2: lip gloss**

| | |
|---|---|
| Polybutene | 86.5% |
| Zeolite containing nitrogen monoxide prepared according to Example 1 using $Zn^{2+}$ as metal cation | 10% |
| Fragrance | 0.5% |
| Pigments | 3% |

**Example 3: lip gloss**

| | |
|---|---|
| Polybutene | 71.5% |
| Octyldodecanol | 15% |
| Zeolite containing nitrogen monoxide prepared according to Example 1 using $Mn^{2+}$ as metal cation | 10% |
| Fragrance | 0.5% |
| Pigments | 3% |

**Example 4: eyelash lacquer**

| | |
|---|---|
| Carnauba wax | 7.7% |
| Paraffin wax | 6% |
| Beeswax | 10.2% |
| Black iron oxide | 2.7% |
| Talc | 2% |
| Bentone 38V | 5.5% |
| Propylene carbonate | 1.83% |
| Zeolite containing nitrogen monoxide prepared | |

| | |
|---|---|
| according to Example 1 using $Zn^{2+}$ as metal cation | 2% |
| Preserving agent | qs |
| Isododecane | qs 100 |

## CLAIMS

1. Cosmetic composition containing at least one dyestuff and nitrogen monoxide adsorbed into a microporous crystalline solid material.

2. Composition according to Claim 1, in which the size of the pores of the microporous crystalline solid material is less than or equal to 1000 Angströms, more preferably less than or equal to 50 Angströms and more preferably less than or equal to 30 Angströms.

3. Composition according to Claim 1 or 2, in which the pores of the microporous crystalline solid material form a repeating three-dimensional network.

4. Composition according to one of the preceding claims, in which the nitrogen monoxide is complexed, in the microporous crystalline solid material, with an organic or mineral cation.

5. Composition according to one of the preceding claims, in which the microporous crystalline solid material is a zeolite of general formula (I) below:

$$[(M_1^{n+})_{x/n}(M_2^{p+})_{y/p}\ldots(M_n^{q+})_{v/q}][Al_zSi_{1-z}O_4] \qquad (I)$$

in which $M_1$ and $M_2$ to $M_n$ are independently chosen from

- metal cations external to the framework independently chosen from the group consisting of Li, Na, K, Mn, Ca, Mg, Fe, Cu, Ru, Rh, Co, Ni, Zn and Ag, and

- organic cations such as $N(R_1)_a(R_2)_b^+$ in which $R_1$ and $R_2$ are independently chosen from H, $-CH_3$, $-CH_2CH_3$ and $-CH_2CH_2CH_3$, and a and b are independently 0, 1, 2, 3 or 4 such that $a + b = 4$,

x ranges from 0 to nz, y ranges from 0 to pz, and v ranges from 0 to qz, on condition that $x/n + y/p +...+ v/q = z$,

z is the number of silicon atoms replaced with aluminium atoms in the zeolite framework,

n+, p+ and q+ are, independently, integers +1, +2 or +3, when the associated cation is a metal cation, or equal to +1 when the associated cation is an organic cation.

6. Composition according to Claim 5, in which $M_1$ and/or $M_2$ represents $NH_4^+$.

7. Composition according to the preceding claim, in which the zeolite has the general formula (II) below:

$$[(M_1^{n+})_{x/n}(M_2^{p+})_{y/p}][Al_zSi_{1-z}O_4] \quad (II)$$

in which $M_1$, $M_2$, z, n+ and p+ are as defined in the preceding claim,

x ranges from 0 to nz, and

y ranges from 0 to pz, on condition that $x/n + y/p = z$.

8. Composition according to either of Claims 5 and 6, in which the metal cations are cations of elements Zn or Mn.

9. Composition according to one of the preceding claims, characterized in that it comprises at least one fatty substance chosen from oils, waxes and pasty fatty substances.

10. Composition according to one of the preceding claims, characterized in that the dyestuff is chosen from mineral dyestuffs.

11. Composition according to one of the preceding claims, characterized in that the dyestuff is chosen from organic dyestuffs.

12. Composition according to one of the preceding claims, characterized in that the dyestuff is chosen from dyes.

13. Composition according to one of the preceding claims, characterized in that the dyestuff is chosen from pigments.

14. Composition according to one of the preceding claims, characterized in that the dyestuff is chosen from lakes.

15. Composition according to Claim 10, in which the dyestuff is chosen from titanium dioxide, optionally surface-treated, zirconium oxide or cerium oxide, iron oxide or chromium oxide, manganese violet, ultramarine blue, chromium hydrate and ferric blue.

16. Composition according to Claim 10, in which the dyestuff is chosen from nitroso, nitro, azo, xanthene, quinoline, anthraquinone, phthalocyanin, metal-complex, isoindolinone, isoindoline,

quinacridone, perinone, perylene, diketopyrrolopyrrole, thioindigo, dioxazine, triphenylmethane and quinophthalone compounds.

17. Composition according to Claim 10, in which at least the dyestuff is a composite pigment composed of particles comprising a mineral core, at least one binder for attaching the organic pigments to the core, and at least one organic pigment at least partially covering the core.

18. Composition according to Claim 11, in which the dyestuff is a lake consisting of a mineral substrate chosen from alumina, silica, calcium sodium borosilicate, calcium aluminium borosilicate and aluminium onto which is adsorbed a dye.

19. Composition according to Claim 10, in which the dyestuff is a pigment with special effects chosen from nacreous pigments, pigments with interference effects not attached to a substrate, fluorescent pigments, phosphorescent pigments, photochromic pigments and thermochromic pigments.

20. Composition according to Claim 19, in which the nacreous pigment(s) is (are) chosen from mica coated with titanium or with bismuth oxychloride, mica coated with titanium and with iron oxides, mica coated with titanium and with ferric blue or chromium oxide, mica coated with titanium and with an organic pigment, and nacreous pigments based on bismuth oxychloride.

21. Composition according to Claim 19, in

which the pigment(s) with interference effects not attached to a substrate are chosen from liquid crystals and holographic interference flakes.

22. Composition according to one of the preceding claims, characterized in that it comprises at least one filler.

23. Composition according to one of the preceding claims, characterized in that it comprises at least one gelling agent.

24. Composition according to one of the preceding claims, characterized in that it comprises fibres.

25. Composition according to one of the preceding claims, characterized in that it comprises a tacky wax.

26. Composition according to one of the preceding claims, characterized in that it is in the form of a makeup product for the lips, the eyelids, the eyelashes, the nails or the skin.

27. Composition according to the preceding claim, characterized in that it is in the form of a lipstick or a mascara.

28. Cosmetic use of a composition according to one of Claims 1 to 26.

29. Cosmetic use of a composition according to one of Claims 1 to 26, for making up the skin, the eyelashes, the eyelids, the lips or the nails.

# INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2006/002663

**A. CLASSIFICATION OF SUBJECT MATTER**
INV. A61K8/19 A61K8/26 A61Q1/00 A61Q19/00

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)
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 practical, search terms used)

EPO-Internal, WPI Data, PAJ, BIOSIS, EMBASE, CHEM ABS Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | WO 2005/003032 A (THE UNIVERSITY COURT OF THE UNIVERSITY OF ST ANDREWS; MORRIS, RUSSELL,) 13 January 2005 (2005-01-13)<br>page 9, line 31 - page 10, line 8<br>page 11, lines 7-12<br>page 11, line 23; claims 18,23,24<br>----- | 1-24 |
| X | WO 03/072039 A (ESSENTIA BIOSYSTEMS, INC; WAUGH, JACOB; DAKE, MICHAEL; ELKINS, CHRISTO) 4 September 2003 (2003-09-04)<br>page 1, line 24 - page 2, line 11<br>page 6, lines 11-16<br>example 2<br>----- | 1-24 |
| A | US 5 184 630 A (JUNG ET AL)<br>9 February 1993 (1993-02-09)<br>the whole document<br>-----<br>-/-- | 1-24 |

☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents :

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"E" earlier document but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"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<br>30 May 2006 | Date of mailing of the international search report<br>07/06/2006 |
| Name and mailing address of the ISA/<br>European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,<br>Fax: (+31-70) 340-3016 | Authorized officer<br>Yon, J-M |

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## INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2006/002663

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| A | US 6 103 275 A (SEITZ ET AL)<br>15 August 2000 (2000-08-15)<br>the whole document<br>----- | 1-24 |

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2006/002663

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| | | CA 2530811 A1 | 13-01-2005 |
| | | EP 1648826 A1 | 26-04-2006 |
| WO 03072039 A | 04-09-2003 | AU 2003213220 A1 | 09-09-2003 |
| | | EP 1482894 A2 | 08-12-2004 |
| | | JP 2005524647 T | 18-08-2005 |
| US 5184630 A | 09-02-1993 | NONE | |
| US 6103275 A | 15-08-2000 | WO 0189572 A1 | 29-11-2001 |
| | | US 7048951 B1 | 23-05-2006 |