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(54) Title: DYE COMPOSITION BASED ON COPOLYMERS DERIVED FROM THE POLYMERIZATION OF AT LEAST ONE CROTONIC ACID MONOMER OR CROTONIC ACID DERIVATIVE AND OF AT LEAST ONE VINYL ESTER MONOMER AND NON-SILICONE FATTY SUBSTANCE, AND PROCESS FOR DYEING KERATIN FIBERS USING SAME

(57) Abstract: The present invention relates to a composition for dyeing keratin fibers, comprising (i) one or more copolymer(s) derived from the polymerization of at least one crotonic acid monomer or crotonic acid derivative and of at least one vinyl ester monomer, the total amount of copolymer(s) of crotonic acid or crotonic acid derivative being at least 1% by weight relative to the weight of the composition, (ii) one or more non-silicone fatty substance(s), the total amount of non-silicone fatty substance(s) being at least 1.5% by weight relative to the total weight of the composition, and (iii) one or more pigments, in which the copolymer is a crotonic acid/vinyl acetate/vinyl neodecanoate terpolymer. The invention also relates to a dyeing process in which said composition is applied to keratin fibers, the operation optionally being followed by drying. The composition makes it possible to obtain temporary dyeing having the advantage of forming a transfer-resistant deposit, leaving the treated fibers individualized, with an improved cosmetic feel.



**DYE COMPOSITION BASED ON COPOLYMERS DERIVED FROM THE
POLYMERIZATION OF AT LEAST ONE CROTONIC ACID MONOMER OR
CROTONIC ACID DERIVATIVE AND OF AT LEAST ONE VINYL ESTER
MONOMER AND NON-SILICONE FATTY SUBSTANCE, AND PROCESS FOR
DYEING KERATIN FIBERS USING SAME**

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The present invention relates to a composition for dyeing keratin fibers, comprising at least one copolymer derived from the polymerization of at least one crotonic acid monomer or crotonic acid derivative and of at least one vinyl ester monomer, at least one non-silicone fatty substance, the total amount of non-silicone fatty substance being at least 0.1% by weight relative to the total weight of the composition, and at least one pigment, and also to a dyeing process using said composition.

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In the field of dyeing keratin fibers, in particular human keratin fibers, it is already known practice to dye keratin fibers via various techniques using direct dyes or pigments for non-permanent dyeing, or dye precursors for permanent dyeing.

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There are essentially three types of process for dyeing the hair:

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a) "permanent" dyeing, the function of which is to afford a substantial modification to the natural color and which uses oxidation dyes which penetrate into the hair fiber and forms the dye via an oxidative condensation process;

b) non-permanent, semi-permanent or direct dyeing, which does not use the oxidative condensation process and withstands four or five shampoo washes; it consists in dyeing keratin fibers with dye compositions containing direct dyes. These dyes are colored and coloring molecules that have affinity for keratin fibers.

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c) temporary dyeing, which gives rise to a modification of the natural color of the hair that remains from one shampoo washing to the next, and which serves to enhance or correct a shade that has already been obtained. It may also be likened to a "makeup" process.

For this last type of dyeing, it is known practice to use colored polymers formed by grafting one or more dyes of azo, triphenylmethane, azine, indoamine or anthraquinone nature onto a polymer chain. These colored polymers are not entirely satisfactory, especially as regards the homogeneity of the coloring obtained and its resistance, not to mention the problems associated with their manufacture and especially with their reproducibility.

Another dyeing method consists in using pigments. Specifically, the use of pigment on the surface of keratin fibers generally makes it possible to obtain visible colorings on dark hair, since the surface pigment masks the natural color of the fiber. The use of pigment for dyeing keratin fibers is described, for example, in patent application FR 2 741 530; when they are applied to keratin fibers, these compositions have the drawback of transferring, i.e. of becoming at least partly deposited, leaving marks, on certain supports with which they may come into contact and in particular clothing or the skin. This results in mediocre persistence of the applied film, making it necessary to regularly repeat the application of the composition. Moreover, the appearance of these unacceptable marks may put certain people off using this type of dyeing.

Compositions for temporarily dyeing and/or making up the hair may also lead to a hair feel that is uncosmetic and/or not natural; the hair thus dyed may in particular lack softness and/or suppleness and/or individualization.

There is thus still a need to obtain compositions for the temporary dyeing of keratin materials, especially the hair, which have the advantage of forming a transfer-resistant deposit, which in particular does not become deposited, at least partly, onto supports with which said compositions are placed in contact, such as the skin (in particular the hands and the face) and/or clothing.

The invention is directed toward providing compositions which do not degrade keratin fibers, which do not impair their cosmetic properties such as softness and suppleness, keep the hair strands clearly individualized, and do not have a coarse feel, while at the same time having transfer-resistance properties.

This aim is achieved with the present invention, one subject of which is a composition for dyeing keratin fibers, especially human keratin fibers such as the hair, comprising at least one copolymer derived from the polymerization of at least one crotonic acid monomer or crotonic acid derivative and of at least one vinyl ester monomer, the total amount of copolymer(s) of crotonic acid or crotonic acid derivative being at least 1% by weight relative to the weight of the composition, at least one non-silicone fatty substance, the total amount of non-silicone fatty substance being at least 1.5% by weight relative to the total weight of the composition, and at least one pigment, and in which the copolymer is a crotonic acid/vinyl acetate/vinyl neodecanoate terpolymer.

A subject of the invention is also a process for dyeing keratin fibers, especially human keratin fibers such as the hair, comprising the application to said fibers of a composition as defined above.

The term "at least one" means "one or more".

The term "comprising a" means "comprising at least one", unless otherwise specified.

One subject of the present invention is thus a composition for dyeing keratin fibers, especially human keratin fibers such as the hair, comprising (i) one or more copolymer(s) derived from the polymerization of at least one crotonic acid monomer or crotonic acid derivative and of at least one vinyl ester monomer, the total amount of copolymer(s) of crotonic acid or crotonic acid derivative being at least 1% by weight relative to the weight of the composition, (ii) one or more non-silicone fatty substance(s), the total amount of non-silicone fatty substance(s) being at least 1.5% by weight relative to the total weight of the composition, and (iii) one or more pigments, in which the copolymer is a crotonic acid/vinyl acetate/vinyl neodecanoate terpolymer.

Dye composition

The composition according to the invention is preferably a cosmetic composition for dyeing keratin fibers, in particular human keratin fibers such as the hair.

It has been observed that by using the composition according to the invention, it is possible to improve the individualization of the hair strands, and also to reduce the transfer. The fibers also have a smoother feel, are softer and more supple, and disentangle more easily.

5 Crotonic acid copolymers

The composition according to the invention comprises at least one copolymer derived from the polymerization of at least one crotonic acid monomer or crotonic acid derivative and of at least one vinyl ester monomer, preferably at least two different vinyl ester monomers.

10 Preferably, the copolymer according to the invention is chosen from copolymers derived from the polymerization of at least one crotonic acid monomer and of at least one vinyl ester monomer, preferably at least two different vinyl ester monomers.

The copolymer of the composition according to the invention is a crotonic acid/vinyl acetate/vinyl neodecanoate terpolymer.

15 The copolymers according to the invention may optionally comprise other monomers such as allylic or methallylic esters, or vinyl ethers. These polymers may optionally be grafted or crosslinked.

Such polymers are described, *inter alia*, in French patent Nos. 1 222 944, 1 580 545, 2 265 782, 2 265 781, 1 564 110 and 2 439 798. Commercial products which fall into this category are the products Resyn® 28-2930 and 28-1310 sold by the company Akzo Nobel (INCI names VA / crotonates / vinyl decanoate copolymer and VA / crotonates copolymer, respectively). Mention
20 may also be made of the products Luviset® CA 66 sold by the company BASF, Aristoflex® A60 sold by the company Clariant (INCI name VA / crotonates copolymer) and Mexomere® PW or PAM sold by the company Chimex (INCI name VA / vinyl butyl benzoate / crotonates copolymer).

25 The total amount of copolymer(s) of crotonic acid or crotonic acid derivative is at least 1% by weight relative to the weight of the composition.

The total amount of copolymer(s) of crotonic acid or crotonic acid derivative according to the invention may range from 1% to 15% by weight relative to the weight of the composition,

preferably from 1% to 10% by weight relative to the weight of the composition, preferably from 1% to 5% by weight relative to the weight of the composition.

Preferably, the crotonic acid/vinyl acetate/vinyl neodecanoate terpolymer is present in an amount ranging from 1% to 15% by weight relative to the weight of the composition, preferably from 1% to 10% by weight relative to the weight of the composition, more preferentially from 1% to 5% by weight relative to the weight of the composition.

Non-silicone fatty substances

As indicated above, the composition contains one or more non-silicone fatty substances.

10 Preferably, the composition contains one or more non-silicone fatty substances that are liquid at 30°C and atmospheric pressure (1.013×10^5 Pa).

According to the present application, the term "fatty substance" means an organic compound that is insoluble in water at 30°C and at atmospheric pressure (1.013×10^5 Pa), i.e. with a solubility of less than 5% by weight, preferably less than 1% by weight and more preferentially less than 0.1% by weight in water. They generally have in their structure at least one hydrocarbon-based chain comprising at least 6 carbon atoms.

The term "non-silicone fatty substance" means a fatty substance not comprising any silicon atoms in its structure.

20 In addition, the fatty substances are generally soluble in organic solvents under the same temperature and pressure conditions, for instance chloroform, dichloromethane, carbon tetrachloride, ethanol, benzene, toluene, tetrahydrofuran (THF) or decamethylcyclopentasiloxane.

The non-silicone fatty substances according to the invention are preferably not fatty acids.

25 Preferably, the non-silicone fatty substances according to the invention do not comprise any C2 to C3 oxyalkylene units or any glycerol units.

The non-silicone fatty substances used in the composition according to the invention are preferably liquid at 30°C, i.e. having a melting point less than or equal to 30°C, at atmospheric pressure (1.013×10^5 Pa).

5 Said non-silicone fatty substances may be chosen from C₆-C₁₆ hydrocarbons, hydrocarbons comprising more than 16 carbon atoms, non-silicone oils of animal origin, oils of triglyceride type of plant or synthetic origin, fluoro oils, liquid fatty alcohols, liquid fatty acid and/or fatty alcohol esters other than triglycerides, and fatty acid ethers.

10 It is recalled that the fatty alcohols, esters and acids more particularly contain at least one saturated or unsaturated, linear or branched hydrocarbon-based group, comprising 6 to 30 and better still from 8 to 30 carbon atoms, which is optionally substituted, in particular, with one or more hydroxyl groups (in particular 1 to 4). If they are unsaturated, these compounds may comprise one to three conjugated or unconjugated carbon-carbon double bonds.

15 As regards the C₆-C₁₆ liquid hydrocarbons, they are linear, branched or optionally cyclic, and are preferably alkanes. Examples that may be mentioned include hexane, cyclohexane, undecane, dodecane, isododecane, tridecane or isoparaffins, such as isohexadecane or isodecane, and mixtures thereof.

The linear or branched hydrocarbons of mineral or synthetic origin comprising more than 16 carbon atoms are preferably chosen from liquid paraffins, petroleum jelly, liquid petroleum jelly, polydecenes and hydrogenated polyisobutene such as Parleam, and mixtures thereof.

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Said non-silicone fatty substances are preferably chosen from liquid C₆-C₁₆ hydrocarbons, linear or branched hydrocarbons of mineral or synthetic origin comprising more than 16 carbon atoms and/or triglyceride oils of plant or synthetic origin.

25 More preferentially, said non-silicone fatty substances are chosen from linear or branched hydrocarbons of mineral origin comprising more than 16 carbon atoms and triglyceride oils of plant origin.

Among the linear or branched hydrocarbons of mineral origin comprising more than 16 carbon atoms, mention may be made especially of liquid paraffins and liquid petroleum jelly.

Among the triglyceride oils of plant origin, mention may be made especially of coconut oil, sweet almond oil, avocado oil, castor oil, coriander oil, olive oil, jojoba oil, sesame oil, groundnut oil, grape seed oil, rapeseed oil, coconut oil, hazelnut oil, shea butter, palm oil, apricot kernel oil, beauty-leaf oil, rice bran oil, maize oil, wheat germ oil, soybean oil, sunflower oil, evening primrose oil, safflower oil, passionflower oil, rye oil or triglycerides of caprylic/capric acids, such as those sold by the company Stéarineries Dubois or those sold under the names Miglyol 810, 812 and 818 by the company Dynamit Nobel.

Preferably, the non-silicone fatty substance is liquid at 30°C and at atmospheric pressure (1.013×10^5 Pa); preferably, the non-silicone fatty substance used is chosen from triglyceride oils of plant origin, preferably coconut oil.

The non-silicone fatty substance(s) are present in a total amount of at least 1.5% by weight relative to the total weight of the composition and better still at least 2% by weight relative to the total weight of the composition.

The total amount of non-silicone fatty substance(s) may range from 1.5% to 15% by weight, preferably from 1.5% to 10% by weight, more preferentially from 1.5% to 7% by weight and better still from 1.5% to 5% by weight relative to the total weight of the composition.

The total amount of non-silicone fatty substance(s) that are liquid at 30°C and at atmospheric pressure may range from 1.5% to 15% by weight, preferably from 1.5% to 10% by weight, more preferentially from 1.5% to 7% by weight and better still from 1.5% to 5% by weight relative to the total weight of the composition.

Preferably, the weight ratio of the total amount of copolymer(s) of crotonic acid or crotonic acid derivative according to the invention to the total amount of non-silicone fatty substance(s) ranges from 0.67 to 15, more preferentially from 0.70 to 10, better still from 0.75 to 10 and better still from 0.75 to 5.

Pigments

The composition comprises one or more pigments.

The term "pigment" is understood to mean white or colored particles of any shape which are insoluble in the composition in which they are present.

The pigments that may be used are especially chosen from the organic and/or mineral pigments known in the art, especially those described in Kirk-Othmer's Encyclopedia of Chemical
5 Technology and in Ullmann's Encyclopedia of Industrial Chemistry.

They may be natural, of natural origin, or not.

These pigments may be in pigment powder or paste form. They may be coated or uncoated.

The pigments may be chosen, for example, from mineral pigments, organic pigments, lakes, pigments with special effects, such as nacres or glitter flakes, and mixtures thereof.

10 The pigment may be a mineral pigment. The term "mineral pigment" means any pigment that satisfies the definition in Ullmann's encyclopedia in the chapter on inorganic pigments. Mention may be made, among mineral pigments of use in the present invention, of ochres, such as red ochre (clay (in particular kaolinite) and iron hydroxide (for example haematite)), brown
ochre (clay (in particular kaolinite) and limonite) or yellow ochre (clay (in particular kaolinite)
15 and goethite); titanium dioxide, optionally surface-treated; zirconium or cerium oxides; zinc, (black, yellow or red) iron or chromium oxides; manganese violet, ultramarine blue, chromium hydrate and ferric blue; or metal powders, such as aluminum powder or copper powder.

Mention may also be made of alkaline earth metal carbonates (such as calcium carbonate or magnesium carbonate), silicon dioxide, quartz and any other compound used as inert filler in
20 cosmetic compositions, provided that these compounds contribute color or whiteness to the composition under the conditions under which they are employed.

The pigment may be an organic pigment. The term "organic pigment" means any pigment that satisfies the definition in Ullmann's encyclopedia in the chapter on organic pigments.

The organic pigment may especially be chosen from nitroso, nitro, azo, xanthene, pyrene,
25 quinoline, anthraquinone, triphenylmethane, fluorane, phthalocyanine, metal-complex, isoindolinone, isoindoline, quinacridone, perinone, perylene, diketopyrrolopyrrole, indigo, thioindigo, dioxazine, triphenylmethane and quinophthalone compounds.

Use may also be made of any mineral or organic compound that is insoluble in the composition and standard in the cosmetics field, provided that these compounds give the composition color or whiteness under the conditions under which they are used, for example guanine, which, according to the refractive index of the composition, is a pigment.

5 In particular, the white or colored organic pigments may be chosen from carmine, carbon black, aniline black, azo yellow, quinacridone, phthalocyanine blue, 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
10 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
15 in patent FR 2 679 771.

Examples that may also be mentioned include pigmentary pastes of organic pigments, such as the products sold by the company Hoechst under the names:

- Cosmenyl Yellow 10G: Pigment Yellow 3 (CI 11710);
- Cosmenyl Yellow G: Pigment Yellow 1 (CI 11680);
- 20 - Cosmenyl Orange GR: Pigment Orange 43 (CI 71105);
- Cosmenyl Red R: Pigment Red 4 (CI 12085);
- Carmine Cosmenyl FB: Pigment Red 5 (CI 12490);
- Cosmenyl Violet RL: Pigment Violet 23 (CI 51319);
- Cosmenyl Blue A2R: Pigment Blue 15.1 (CI 74160);
- 25 - Cosmenyl Green GG: Pigment Green 7 (CI 74260);
- Cosmenyl Black R: Pigment Black 7 (CI 77266).

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, which provides for the attachment of the organic pigments to the core, and at least one organic pigment which at least partially covers the core.

The organic pigment may also be a lake. The term “lake” 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 aluminum borosilicate and aluminum.

Among the dyes, mention may be made of carminic acid. Mention may also be made of the dyes 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 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).

Mention may be made, as examples of lakes, of the product known under the following name: D&C Red 7 (CI 15 850:1).

The pigment may also be a pigment with special effects. The term “pigments with special effects” means pigments that generally create a colored 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 thus contrast with colored pigments that afford a standard uniform opaque, semi-transparent or transparent shade.

Several types of pigment with special effects exist: those with a low refractive index, such as fluorescent or photochromic pigments, and those with a high refractive index, such as nacres, interference pigments or glitter flakes.

Examples of pigments with special effects that may be mentioned include nacreous pigments such as mica coated with titanium or with bismuth oxychloride, colored 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 of the abovementioned type, and also nacreous pigments based on bismuth oxychloride. Nacreous pigments that may be mentioned include the Cellini nacres sold by Engelhard (mica-TiO₂-lake), Prestige sold by Eckart (mica-TiO₂), Prestige Bronze sold by Eckart (mica-Fe₂O₃),
5 and Colorona sold by Merck (mica-TiO₂-Fe₂O₃).

Mention may be made of the gold-colored nacres sold especially by the company Engelhard under the name Brilliant gold 212G (Timica), Gold 222C (Cloisonne), Sparkle gold (Timica), Gold 4504 (Chromalite) and Monarch gold 233X (Cloisonne); the bronze nacres sold especially by the company Merck under the name Bronze fine (17384) (Colorona) and Bronze (17353)
10 (Colorona) and by the company Engelhard under the name Super bronze (Cloisonne); the orange nacres sold especially by the company Engelhard under the name Orange 363C (Cloisonne) and Orange MCR 101 (Cosmica) and by the company Merck under the name Passion orange (Colorona) and Matte orange (17449) (Microna); the brown nacres sold especially by the company Engelhard under the name Nu-antique copper 340XB (Cloisonne)
15 and Brown CL4509 (Chromalite); the nacres with a coppery glint sold especially by the company Engelhard under the name Copper 340A (Timica); the nacres with a red glint sold especially by the company Merck under the name Sienna fine (17386) (Colorona); the nacres with a yellow glint sold especially by the company Engelhard under the name Yellow (4502) (Chromalite); the red nacres with a gold glint sold especially by the company Engelhard under
20 the name Sunstone G012 (Gemtone); the pink nacres sold especially by the company Engelhard under the name Tan opale G005 (Gemtone); the black nacres with a gold glint sold especially by the company Engelhard under the name Nu antique bronze 240 AB (Timica), the blue nacres sold especially by the company Merck under the name Matte blue (17433) (Microna), the white nacres with a silvery glint sold especially by the company Merck under the name Xirona Silver,
25 and the golden-green pink-orange nacres sold especially by the company Merck under the name Indian summer (Xirona), and mixtures thereof.

Still as examples of nacres, mention may also be made of particles comprising a borosilicate substrate coated with titanium oxide.

Particles comprising a glass substrate coated with titanium oxide are sold in particular under
30 the name Metashine MC1080RY by the company Toyal.

Finally, examples of nacres that may also be mentioned include polyethylene terephthalate flakes, especially those sold by the company Meadowbrook Inventions under the name Silver 1P 0.004X0.004 (silver flakes).

5 It is also possible to envisage multilayer pigments based on synthetic substrates, such as alumina, silica, calcium sodium borosilicate, calcium aluminum borosilicate and aluminum.

The pigments with special effects may also be chosen from reflective particles, i.e. especially from particles whose size, structure, especially the thickness of the layer(s) of which they are made and their physical and chemical nature, and surface state, allow them to reflect incident light. This reflection may, if appropriate, have an intensity sufficient to create, at the surface of
10 the composition or mixture, when the latter is applied to the substrate to be made up, highlight points visible to the naked eye, that is to say more luminous points which contrast with their surroundings by appearing to sparkle.

The reflective particles may be selected so as not to significantly alter the coloring effect generated by the coloring agents with which they are combined, and more particularly so as to
15 optimize this effect in terms of color rendition. They may more particularly have a yellow, pink, red, bronze, orange, brown, gold and/or coppery color or glint.

These particles may have varied forms and may especially be in platelet or globular form, in particular in spherical form.

Irrespective of their form, the reflective particles may or may not have a multilayer structure,
20 and, in the case of a multilayer structure, may have, for example, at least one layer of uniform thickness, especially of a reflective material.

When the reflective particles do not have a multilayer structure, they may be composed, for example, of metal oxides, especially titanium or iron oxides obtained synthetically.

When the reflective particles have a multilayer structure, they may comprise, for example, a
25 natural or synthetic substrate, especially a synthetic substrate at least partially coated with at least one layer of a reflective material, especially of at least one metal or metallic material. The substrate may be made of one or more organic and/or mineral materials.

More particularly, it may be chosen from glasses, ceramics, graphite, metal oxides, aluminas, silicas, silicates, especially aluminosilicates and borosilicates, and synthetic mica, and mixtures thereof, this list not being limiting.

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

- 5 Reflective particles are described in particular in the documents

JP-A-09188830, JP-A-10158450, JP-A-10158541, JP-A-07258460 and JP-A-05017710.

Mention may also be made, still by way of example of reflective particles comprising a mineral substrate coated with a layer of metal, of the particles comprising a borosilicate substrate coated with silver.

- 10 Particles comprising a glass substrate coated with silver, in the form of platelets, are sold under the name Microglass Metashine REFSX 2025 PS by 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.

- 15 Use may also be made of particles comprising a metal substrate, such as silver, aluminum, iron, chromium, nickel, molybdenum, gold, copper, zinc, tin, magnesium, steel, bronze or titanium, said substrate being coated with at least one layer of at least one metal oxide, such as titanium oxide, aluminum oxide, iron oxide, cerium oxide, chromium oxide, silicon oxides and mixtures thereof.

- 20 Examples that may be mentioned include aluminum powder, bronze powder or copper powder coated with SiO₂ sold under the name Visionaire by the company Eckart.

- 25 Mention may also be made of pigments with an interference effect which are not attached to a substrate, such as liquid crystals (Helicones HC from Wacker) or interference holographic glitter (Geometric Pigments or Spectra f/x from Spectratek). Pigments with special effects also comprise fluorescent pigments, whether these are substances that are fluorescent in daylight or that produce an ultraviolet fluorescence, phosphorescent pigments, photochromic pigments, thermochromic pigments and quantum dots, sold, for example, by the company Quantum Dots Corporation.

Quantum dots are luminescent semiconductive nanoparticles capable of emitting, under light excitation, irradiation with a wavelength of between 400 nm and 700 nm. These nanoparticles are known from the literature. In particular, they may be synthesized according to the processes described, for example, in US 6 225 198 or US 5 990 479, in the publications cited therein and
5 also in the following publications: Dabboussi B.O. et al., “(CdSe)ZnS core-shell quantum dots: synthesis and characterisation of a size series of highly luminescent nanocrystallites”, Journal of Physical Chemistry B, vol. 101, 1997, pp. 9463-9475, and Peng, Xiaogang et al., “Epitaxial growth of highly luminescent CdSe/CdS core/shell nanocrystals with photostability and electronic accessibility”, Journal of the American Chemical Society, vol. 119, No. 30, pp. 7019-
10 7029.

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

The size of the pigment used in the cosmetic composition according to the present invention is
15 generally between 10 nm and 200 μm , preferably between 20 nm and 80 μm and even more preferably between 30 nm and 50 μm .

The pigments may be dispersed in the product by means of a dispersant.

The dispersant serves to protect the dispersed particles against their agglomeration or flocculation. This dispersant may be a surfactant, an oligomer, a polymer or a mixture of several
20 thereof, bearing one or more functionalities with strong affinity for the surface of the particles to be dispersed. In particular, they may become physically or chemically attached to the surface of the pigments. These dispersants also contain at least one functional group that is compatible with or soluble in the continuous medium. In particular, 12-hydroxystearic acid esters and C8 to C20 fatty acid esters of polyols such as glycerol or diglycerol are used, such as poly(12-
25 hydroxystearic acid) acid stearate with a molecular weight of about 750 g/mol, such as the product sold under the name Solsperse 21 000 by the company Avecia, polyglyceryl-2 dipolyhydroxystearate (CTFA name) sold under the reference Dehymyls PGPH by the company Henkel, or polyhydroxystearic acid such as the product sold under the reference Arlcel P100 by the company Uniqema, and mixtures thereof.

As other dispersants that may be used in the compositions of the invention, mention may be made of quaternary ammonium derivatives of polycondensed fatty acids, for instance Solsperse 17 000 sold by the company Avecia, and polydimethylsiloxane/oxypropylene mixtures such as those sold by the company Dow Corning under the references DC2-5185 and DC2-5225 C.

- 5 The pigments used in the cosmetic composition according to the invention may be surface-treated with an organic agent.

Thus, the pigments that have been surface-treated beforehand, which are useful in the context of the invention, are pigments that have totally or partially undergone a surface treatment of chemical, electronic, electrochemical, mechanochemical or mechanical nature, with an organic agent such as those described especially in *Cosmetics and Toiletries*, February 1990, Vol. 105, pages 53-64, before being dispersed in the composition in accordance with the invention. These organic agents may be chosen, for example, from waxes, for example carnauba wax and beeswax; fatty acids, fatty alcohols and derivatives thereof, such as stearic acid, hydroxystearic acid, stearyl alcohol, hydroxystearyl alcohol and lauric acid and derivatives thereof; anionic surfactants; lecithins; sodium, potassium, magnesium, iron, titanium, zinc or aluminum salts of fatty acids, for example aluminum stearate or laurate; metal alkoxides; polyethylene; (meth)acrylic polymers, for example polymethyl methacrylates; polymers and copolymers containing acrylate units; alkanolamines; silicone compounds, for example silicones, polydimethylsiloxanes; organofluorine compounds, for example perfluoroalkyl ethers; fluorosilicone compounds.

The surface-treated pigments that are useful in the cosmetic composition according to the invention may also have been treated with a mixture of these compounds and/or may have undergone several surface treatments.

The surface-treated pigments that are useful in the context of the present invention may be prepared according to surface-treatment techniques that are well known to those skilled in the art, or may be commercially available in the required form.

Preferably, the surface-treated pigments are coated with an organic layer.

The organic agent with which the pigments are treated may be deposited on the pigments by evaporation of solvent, chemical reaction between the molecules of the surface agent or creation of a covalent bond between the surface agent and the pigments.

The surface treatment may thus be performed, for example, by chemical reaction of a surface agent with the surface of the pigments and creation of a covalent bond between the surface agent and the pigments or the fillers. This method is especially described in patent US 4 578 266.

- 5 An organic agent covalently bonded to the pigments will preferably be used.

The agent for the surface treatment may represent from 0.1% to 50% by weight, preferably from 0.5% to 30% by weight and even more preferentially from 1% to 10% by weight relative to the total weight of the surface-treated pigment.

Preferably, the surface treatments of the pigments are chosen from the following treatments:

- 10 - a PEG-silicone treatment, for instance the AQ surface treatment sold by LCW;
- a methicone treatment, for instance the SI surface treatment sold by LCW;
- a dimethicone treatment, for instance the Covasil 3.05 surface treatment sold by LCW;
- a dimethicone/trimethyl siloxysilicate treatment, for instance the Covasil 4.05 surface treatment sold by LCW;
- 15 - a magnesium myristate treatment, for instance the MM surface treatment sold by LCW;
- an aluminum dimyristate treatment, such as the MI surface treatment sold by Miyoshi;
- a perfluoropolymethylisopropyl ether treatment, for instance the FHC surface treatment sold by LCW;
- an isostearyl sebacate treatment, for instance the HS surface treatment sold by Miyoshi;
- 20 - a perfluoroalkyl phosphate treatment, for instance the PF surface treatment sold by Daito;
- an acrylate/dimethicone copolymer and perfluoroalkyl phosphate treatment, for instance the FSA surface treatment sold by Daito;
- a polymethylhydrogenosiloxane/perfluoroalkyl phosphate treatment, for instance the FS01 surface treatment sold by Daito;

- an acrylate/dimethicone copolymer treatment, for instance the ASC surface treatment sold by Daito;

- an isopropyl titanium triisostearate treatment, for instance the ITT surface treatment sold by Daito;

5 - an acrylate copolymer treatment, for instance the APD surface treatment sold by Daito;

- a perfluoroalkyl phosphate/isopropyl titanium triisostearate treatment, for instance the PF + ITT surface treatment sold by Daito.

Preferably, the pigment is chosen from mineral or mixed mineral-organic pigments.

10 The amount of pigment(s) may range from 0.01% to 30% by weight, more particularly from 0.05% to 20% by weight, preferably from 0.1% to 15% by weight and preferably from 1% to 10% by weight relative to the total weight of the composition.

The composition of the invention may contain colored or coloring species other than the pigments according to the invention, such as direct dyes or dye precursors.

15 Thickener

According to a preferred embodiment, the composition according to the invention comprises at least one thickener, preferably chosen from natural polymers, carboxyvinyl polymers such as homopolymers or copolymers of acrylic and/or methacrylic acid and/or ester, which are preferably crosslinked, crosslinked thickening polyacrylamides and associative polymers
20 comprising at least one hydrophilic unit and at least one fatty chain.

According to the present invention, the term "thickener" refers to a compound which, by its presence at a concentration of 0.05% by weight, increases the viscosity of a composition into which it is introduced by at least 20 cps, preferably by at least 50 cps, at room temperature (25°C), at atmospheric pressure and at a shear rate of 1 s^{-1} (the viscosity may be measured using
25 a cone/plate viscometer, a Haake R600 rheometer or the like).

The thickener(s) may be chosen especially from carboxyvinyl polymers such as crosslinked acrylic acid homopolymers (carbomer) such as those sold under the name Carbopol by the

company Goodrich, polyacrylates and polymethacrylates such as the products sold under the names Lubrajel or Norgel by the company Guardian or under the name Hispagel by the company Hispano Chimica; polyacrylamides such as the product sold under the name Sepigel 305 by the company SEPPIC; polysaccharides such as alginates, cellulose and derivatives thereof, especially carboxymethylcellulose, hydroxymethylcellulose, hydroxypropylcellulose and microcrystalline cellulose; natural gums such as xanthan gum, guar gum, locust bean gum, acacia gum, scleroglucans, chitin and chitosan derivatives, carrageenans; or clays such as montmorillonite, bentones and magnesium aluminum silicates (Veegum).

- 10 According to a particular embodiment of the invention, the composition comprises at least one thickener chosen from crosslinked acrylic and/or methacrylic acid polymers.

According to a particular embodiment of the invention, the composition comprises at least one thickener chosen from crosslinked acrylic acid homopolymers.

- 15 The thickener may be present in the composition in a total content ranging from 0.01% to 10% by weight relative to the weight of the composition, preferably from 0.1% to 5% by weight relative to the weight of the composition, preferably from 0.4% to 2% by weight relative to the weight of the composition.

- 20 The composition according to the invention advantageously comprises water, which may preferably be present in a content ranging from 20% to 98% by weight relative to the weight of the composition.

Additives

- 25 The compositions may also comprise at least one agent commonly used in cosmetics, for example chosen from reducing agents, fatty substances other than the non-silicone fatty substances mentioned above, organic solvents, softeners, antifoams, moisturizers, UV-

screening agents, peptizers, solubilizers, fragrances, anionic, cationic, nonionic or amphoteric surfactants, proteins and vitamins.

The above additives are generally present in an amount for each of them of between 0.01% and 20% by weight relative to the weight of the composition.

- 5 Needless to say, a person skilled in the art will take care to choose this or these optional additive(s) so that the advantageous properties intrinsically attached to the formation of the sheathing in accordance with the invention are not, or not substantially, detrimentally affected.

Presentation form

- 10 The composition according to the invention may especially be in the form of a suspension, a dispersion, 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 mousse, a stick, a dispersion of vesicles, especially of ionic or nonionic lipids, or a two-phase or multi-phase lotion. Preferably, the composition is in the form of a gel.

15

A person skilled in the art may select the appropriate presentation form, and also the method for preparing it, on the basis of his general knowledge, taking into account first the nature of the constituents used, especially their solubility in the support, and secondly the application envisaged for the composition.

20

Organic solvents

The composition according to the invention may comprise one or more organic solvents.

- 25 Examples of organic solvents that may be mentioned include lower C₁-C₄ alkanols, such as ethanol and isopropanol; polyols and polyol ethers, for instance 2-butoxyethanol, propylene glycol, propylene glycol monomethyl ether and diethylene glycol monoethyl ether and

monomethyl ether, and also aromatic alcohols, for instance benzyl alcohol or phenoxyethanol, and mixtures thereof.

Preferably, the composition according to the invention comprises one or more organic solvents.

5

When they are present, the organic solvents are present in proportions preferably inclusively between 0.1% and 40% by weight approximately relative to the total weight of the dye composition, more preferentially between 1% and 30% by weight approximately and even more particularly inclusively between 5% and 25% by weight relative to the total weight of the composition.

10

Process

The composition described above may be used on wet or dry keratin fibers, and also on any type of fair or dark, natural or dyed, permanent-waved, bleached or relaxed fibers.

15 The application to the keratin fibers may be performed via any standard means, in particular using a comb, a fine brush, a coarse brush or with the fingers.

After application of the composition, the fibers may be left to dry naturally or dried, for example at a temperature above or equal to 30°C. The drying, if it is performed, may be performed immediately after the application. Preferably, if the fibers are dried, they are dried, in addition
20 to supplying heat, with a flow of air.

During drying, a mechanical action may be exerted on the locks, such as combing, brushing or running the fingers through. This operation may similarly be performed once the fibers have been dried, naturally or otherwise.

The drying step of the process of the invention may be performed with a hood, a hairdryer, a
25 straightening iron, a Climazon, etc.

When the drying step is performed with a hood or a hairdryer, the drying temperature is between 30°C and 110°C and preferably between 50 and 90°C.

When the drying step is performed with a straightening iron, the drying temperature is between 110 and 220°C and preferably between 140 and 200°C.

5 EXAMPLES

Composition examples:

Example 1:

Compositions (g AM/100 g)

10

	A1	B1	C1
	COMPARATIVE	COMPARATIVE	INVENTION
VA/crotonates/vinyl neodecanoate copolymer	2	2	2
Neutralizer (aminomethylpropanol)	qs	qs	qs
Carbomer	0.75	0.75	0.75
Mica (and) titanium dioxide	10	10	10
Phenoxyethanol	0.7	0.7	0.7
Ethanol	7.5	7.5	7.5
PEG-40 Hydrogenated castor oil	1	1	1
Propylene glycol	-	2	-
<i>Cocos nucifera</i> oil	-	-	2
Water	qs 100	qs 100	qs 100

Protocol

Composition A1, B1 or C1 is applied to locks of yack hair at a rate of 1 g of composition per
 5 gram of lock.

After application, the locks are combed, dried with a hairdryer and then combed.

Results: "cosmetic feel" performance

10

The performance qualities in terms of cosmetic feel were evaluated on dry hair by five experts, in a blind test.

In 100% of the cases, the experts judged that composition C1 according to the invention,
 compared with compositions A1 and B1, afforded smooth locks with clearly individualized hair
 15 strands, having a pleasant cosmetic feel, especially good softness, good suppleness and absence of tackiness.

Example 2:

20 **Compositions** (g AM/100 g)

	A2	B2	C2
	Invention	comparative	comparative
Phenoxyethanol	0.7	0.7	0.7
<i>Cocos nucifera</i> oil	2.5	2.5	2.5
CI 77891 (and) synthetic fluorophlogopite (and) CI 15850	10	10	10

VA/crotonates/vinyl neodecanoate copolymer	3	-	-
Carbomer	0.75	0.75	0.75
Polyvinylcaprolactam	-	3	-
VP/dimethylaminoethyl methacrylate copolymer	-	-	3
Ethanol	7.5	7.5	7.5
Neutralizer (triethanolamine and/or aminomethylpropanol)	qs	qs	qs
PEG-40 Hydrogenated castor oil	1	1	1
Water	qs 100	qs 100	qs 100

Protocol

Composition A2, B2 or C2 is applied to locks of yack hair at a rate of 1 g of composition per
5 gram of lock.

The locks are dried with a hairdryer and then combed.

The locks are then rubbed on a white cloth.

Results: "transfer-resistance" performance

10

The performance qualities in terms of transfer resistance were evaluated by five experts, in a blind test, who visually evaluated the amount of pigment present on the white cloth after rubbing.

In 100% of the cases, the experts judged that composition A2 according to the invention, compared with compositions B2 and C2, led to a very markedly smaller amount of pigment present on the cloth than the amount deposited on the cloth by each of compositions B2 and C2. Composition A according to the invention thus has better transfer-resistance properties than the comparative compositions B2 and C2.

Example 3:

Compositions (g AM/100 g)

	A4 INVENTION	E Comparative
VA/crotonates/vinyl neodecanoate copolymer	3	-
Vinyl acetate / crotonic acid /vinyl t-butyl-4-benzoate	-	3
Neutralizer (aminomethylpropanol and/or triethanolamine)	qs	qs
Carbomer	0.75	0.75
CI 77891 (and) synthetic fluorphlogopite (and) CI 15850	10	10
Phenoxyethanol	0.7	0.7
Ethanol	7.5	7.5
PEG-40 Hydrogenated castor oil	1	1
<i>Cocos nucifera</i> oil	2	2
Water	qs 100	qs 100

Protocol

Composition A4 and composition E are applied to locks of yack hair at a rate of 1 g of composition per gram of lock.

After application, the locks are combed, dried with a hairdryer and then combed again.

Results: “transfer-resistance” performance

- 5 In order to evaluate the “transfer-resistance” performance, the locks of hair are combed 4 times over a sheet of white paper. The residues obtained are then collected. They are weighed with a precision balance (precision level 0.1 mg).

The higher the quantity of residues collected is, the greater the transfer will be.

The results obtained are disclosed herewith:

	Quantity of residues collected (in mg)
A4 Invention	13,3 mg
E Comparative	21,2 mg

10

The amount of residues transferred after the passage of the comb is lower for the locks treated with composition A4 according to the invention, compared to the locks treated with comparative composition E.

- 15 Therefore, the composition A4 according to the invention has higher “transfer-resistance” properties than comparative composition E.

CLAIMS

1. A composition comprising (i) one or more copolymers derived from the polymerization of at least one crotonic acid monomer or crotonic acid derivative and of at least one vinyl ester monomer, the total amount of copolymer(s) of crotonic acid or crotonic acid derivative being at least 1% by weight relative to the weight of the composition,
- (ii) one or more non-silicone fatty substance(s), the total amount of non-silicone fatty substance(s) being at least 1.5% by weight relative to the total weight of the composition, and
- (iii) one or more pigments,
- in which the copolymer is a crotonic acid/vinyl acetate/vinyl neodecanoate terpolymer.
2. The composition as claimed in claim 1, characterized in that said copolymer(s) also comprise other monomers such as allylic or methallylic esters or vinyl ethers.
3. The composition as claimed in either of the preceding claims, in which said copolymer derived from the polymerization of at least one crotonic acid monomer or crotonic acid derivative and of at least one vinyl ester monomer is present in an amount ranging from 1% to 15% by weight relative to the weight of the composition, preferably from 1% to 10% by weight relative to the weight of the composition, preferably from 1% to 5% by weight relative to the total weight of the composition.
4. The composition as claimed in any one of the preceding claims, characterized in that the non-silicone fatty substance(s) are liquid at 30°C and at atmospheric pressure (1.013×10^5 Pa).
5. The composition as claimed in any one of the preceding claims, characterized in that the non-silicone fatty substance(s) are chosen from C₆-C₁₆ hydrocarbons, linear or branched hydrocarbons of mineral or synthetic origin comprising more than 16 carbon atoms and/or

triglyceride oils of plant or synthetic origin, preferably from C₆-C₁₆ hydrocarbons, linear or branched hydrocarbons of mineral or synthetic origin comprising more than 16 carbon atoms and/or triglyceride oils of plant or synthetic origin, better still from linear or branched hydrocarbons of mineral origin comprising more than 16 carbon atoms and triglyceride oils of plant origin.

6. The composition as claimed in any one of the preceding claims, characterized in that the non-silicone fatty substance(s) are chosen from triglyceride oils of plant origin.

7. The composition as claimed in any one of the preceding claims, characterized in that the non-silicone fatty substance is coconut oil.

8. The composition as claimed in any one of the preceding claims, characterized in that said non-silicone fatty substance is present in a total amount of at least 2% by weight relative to the total weight of the composition.

9. The composition as claimed in any one of the preceding claims, characterized in that it also comprises a thickener, preferably chosen from crosslinked copolymers of acrylic and/or methacrylic acid, preferably from crosslinked acrylic acid homopolymers.

10. A process for the cosmetic treatment of, in particular for dyeing, keratin fibers, in particular human keratin fibers such as the hair, in which the composition as defined according to any one of claims 1 to 9 is applied to said fibers.

11. The use of the composition as defined according to any one of claims 1 to 9, for the cosmetic treatment, in particular dyeing, of keratin fibers, in particular human keratin fibers such as the hair.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2018/061571

A. CLASSIFICATION OF SUBJECT MATTER

INV. A61K8/81 A61Q5/06 A61K8/92
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

A61K A61Q

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

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

EPO-Internal, WPI Data, 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.
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X	FR 2 741 530 A1 (OREAL [FR]) 30 May 1997 (1997-05-30)	1-4,8-11
Y	page 2, line 12 - page 6, line 21; claims; examples 1,2,3 page 10, line 15 - page 11, line 24 page 13, line 4 - line 13 -----	5-7
Y	FR 2 750 601 A1 (OREAL [FR]) 9 January 1998 (1998-01-09) page 1, line 29 - page 7, line 11; examples page 9, line 29 - page 10, line 16 page 14, line 15 - page 16, line 26 ----- -/-	5-7



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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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

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INTERNATIONAL SEARCH REPORT

International application No

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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A	FR 2 758 719 A1 (OREAL [FR]) 31 July 1998 (1998-07-31) page 1, line 36 - page 5, line 2; claims; example 1 page 10, line 5 - line 40 -----	1-11
A	EP 0 945 130 A2 (OREAL [FR]) 29 September 1999 (1999-09-29) Emulsion A,B; paragraph [0036] - paragraphs [0038], [0082] -----	1-11

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